ISTCP-X

BOOK OF ABSTRACTS

10th Congress of the International Society of Theoretical Chemical Physics

Tromsø, 11-17 July 2019

THE ARCTIC UNIVERSITY OF NORWAY • UIT •

WELCOME

On behalf of the scientific committee and the local organizing committee, it is a great pleasure for me to welcome you all to Tromsø and the **10th Congress of the International Society of Theoretical Chemical Physics (ISTCP-X).** 540 participants from around the world can explore the latest advances in the field of theoretical chemical physics through more than 200 talks and 270 posters. The midnight sun will further stimulate scientific discussions into the late hours of the night.

The compact conference venue at Clarion Hotel The Edge, and the vicinity to the pulsating city life of Tromsø, will give the participants ample opportunity to enjoy both the science at the conference and the unique atmosphere of the city of Tromsø.

This year, Tromsø celebrates is 225th anniversary as a city. Tromsø is a city in growth and has now more than 75000 inhabitants. It is often referred to as the Gateway to the Arctic, as many arctic expeditions were launched from Tromsø. Throughout the city, you can see remnants of the history of the city as a port for harvesting the rich natural resources of the Arctic ocean that has been the basis for the prosperity of the city.

Today, Tromsø is perhaps more characterized by being a university city, hosting the main campus of the University of Tromsø – The Arctic University of Norway, the world's northernmost university with almost 17000 students. Theoretical chemistry has been a research field at the university since the first students arrived in Tromsø in 1972. This activity is today integrated in the Hylleraas Centre for Quantum Molecular Sciences, a Norwegian Centre of Excellence shared with and led by the University of Oslo, and involves around 25 staff members, postdocs, PhD and Master students here in Tromsø.

I once again welcome you to Tromsø and the ISTCP-X. I hope you will enjoy your stay at this unique location close to the Arctic, and that the conference will give a lot of new scientific ideas and some lasting memories from our city and Northern Norway.

Kenneth Ruud

Kenneth Ruud, Chair of ISTCP-X

Sponsors

The Research Council of Norway

Hylleraas

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ACS OMEGA

JCTC Journal of Chemical Theory and Computation

THE JOURNAL OF PHYSICAL CHEMISTRY A/B/C

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Journal of COMPUTATIONAL CHEMISTRY

International Journal of QUANTUM CHEMISTRY

NON SOLUS
ELSEVIER

PCCP
Physical Chemistry Chemical Physics

SCIENTIFIC COMMITTEE

Erkki Brändas (Uppsala University, Sweden, **Co-chair**)
Aurora Clark (Washington State University, USA)
David Clary (University of Oxford, UK)
Hazel Cox (University of Sussex, UK)
Peter Gill (Australian National University, Australia)
Leticia Gonzalez (University of Vienna, Austria)
Kersti Hermansson (Uppsala University, Sweden)
Bogumil Jeziorski (University of Warsaw, Poland)
Anna Krylov (University of Southern California, USA)
Shuhua Li (Nanjing University, China)
Hiromi Nakai (Waseda University, Japan)
Oleg Prezhdo (University of Southern California, USA)
Kenneth Ruud (UiT The Arctic University of Norway, Norway, **Chair**)
Thereza Soares (Universidade Federal de Pernambuco, Brazil)

LOCAL ORGANIZING COMMITTEE

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Kenneth Ruud (**Chair**)

WEB MASTER

Michal Repisky (UiT The Arctic University of Norway)

LOGO DESIGN

Karen O.H. Dundas (UiT The Arctic University of Norway)

SESSION CHAIRS

From picoseconds to attoseconds: nuclear and electron dynamics

David Clary (University of Oxford, UK)
Leticia Gonzalez (University of Vienna, Austria)
Fernando Martin (Universidad Autónoma de Madrid, Spain)

Aspects of heavy-element chemistry

Pekka Pyykkö (University of Helsinki, Finland)
Trond Saue (University Toulouse III-Paul Sabatier, France)

Emergent electronic structure methods

Stefan Goedecker (University of Basel, Switzerland)
Gustavo Scuseria (Rice University, USA)

Multiscale modelling including focussed models

Benedetta Mennucci (University of Pisa, Italy)
Lyudmila Slipchenko (Purdue University, USA)

Large-scale electronic structure models of materials

Thomas Heine (Universität Leipzig, Germany)
Hiromi Nakai (Waseda University, Japan)

Ultracold chemical physics

Jeremy M. Hutson (Durham University, UK)
Bogumil Jeziorski (University of Warsaw, Poland)

Molecular properties and interactions

Antonio Rizzo (CNR Pisa, Italy)
Krzysztof Szalewicz (University of Delaware, USA)

Computational spectroscopy: From X-rays to microwaves

Attila Csaszar (Eötvös Loránd University, Hungary)
Hans Ågren (KTH, Stockholm, Sweden)

90 years of r12: Hylleraas symposium

Wim Klopper (Karlsruher Institut für Technologie, Germany)
Ed Valeev (Virginia Tech, Blacksburg (VA), USA)

Machine learning and data-driven approaches in chemical physics
Alán Aspuru-Guzik (University of Toronto, Canada)
Pavlo Dral (Max-Planck Institut für Kohlenforschung, Mülheim, Germany)

Computational biophysics
Fernanda Duarte (University of Oxford, UK)
Ursula Röthlisberger (L'École Polytechnique Fédérale de Lausanne, Switzerland)

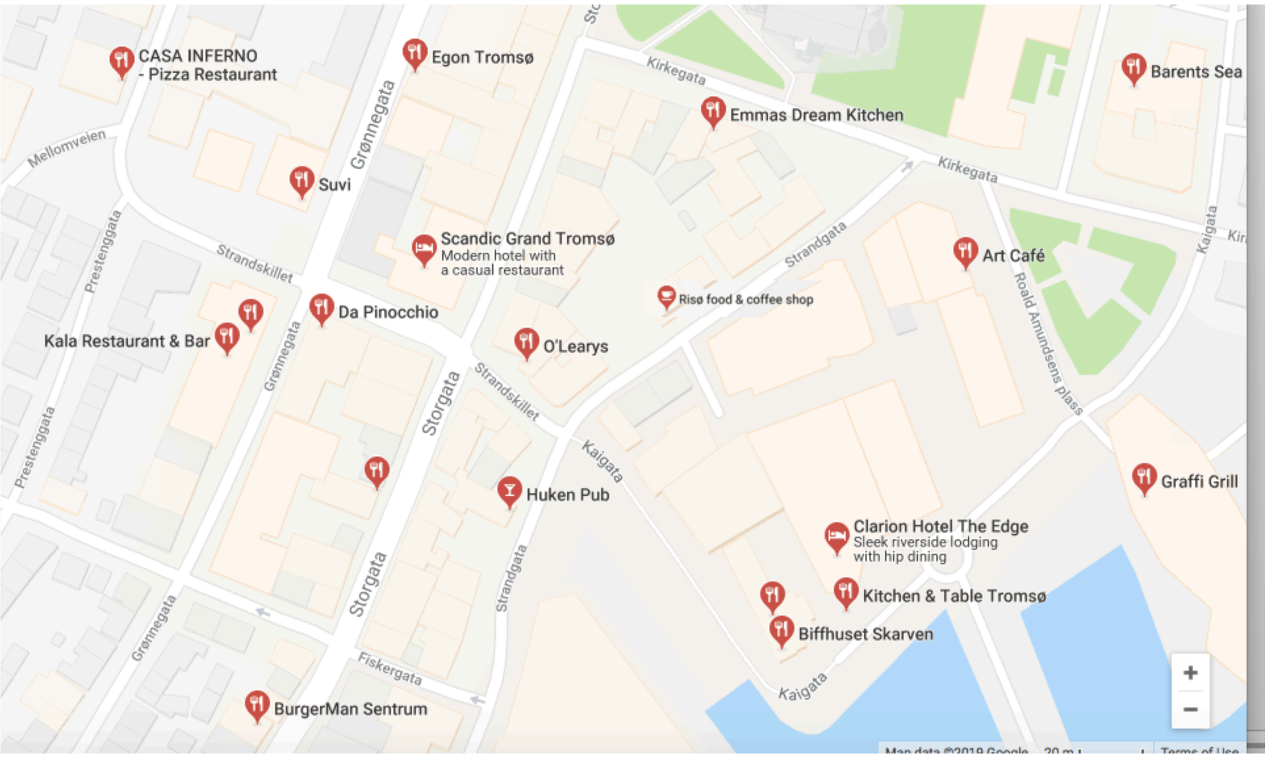
Path-integral methods
David E. Manolopoulos (University of Oxford, UK)
Gregory Voth (University of Chicago, USA)

Physical organic chemistry and catalysis
Odile Eisenstein (Institut Charles Gerhardt Montpellier, France)
Vidar R. Jensen (University of Bergen, Norway)

Janos Ladik memorial symposium
Erkki Brändas (Uppsala University, Sweden)
Kenneth Ruud (UiT The Arctic University of Norway, Norway)

Places to eat in downtown Tromsø

Downtown South



Map data ©2018 Google

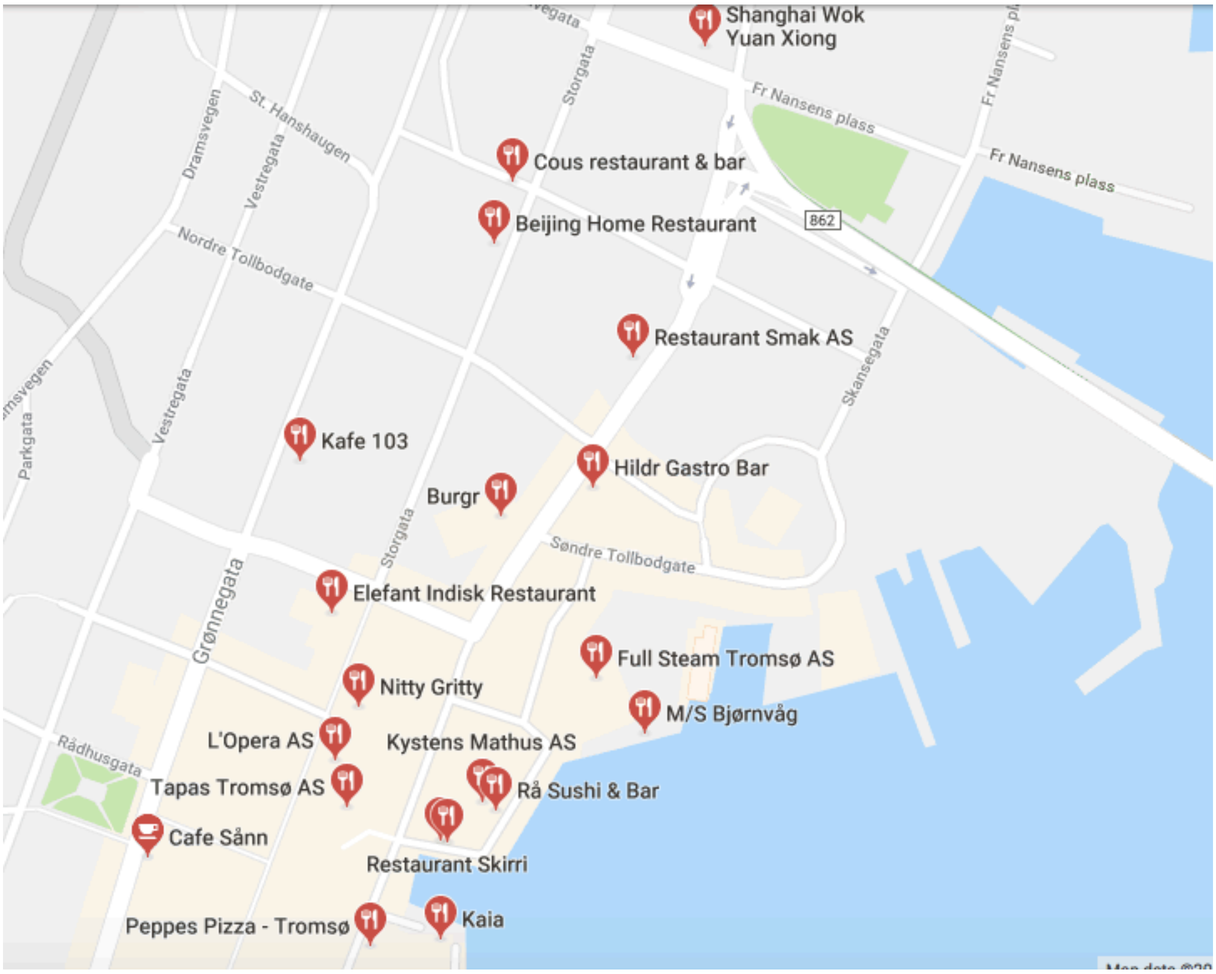
Casa Inferno *Italian cuisine, wine*	**Huken Brygg** *Gastropub*	**Blårock cafe** *Hamburgers, pub*
Egon *Family style dining*	**Burgerman** *Hamburgers*	**Art Cafe** *Homestyle cooking*
Suvi *Vietnamese/Sushi*	**Emmas Dream Kitchen** *Fine dining, local ingredients*	**Graffi Grill** *Burgers and grilled food*
Da Pinocchio (now **East)** *Asian food*	**Risø** *Light food and coffee*	**Rå** *Sushi*
Kala *Asian contemporary dining*	**Biffhuset Skarven** *Steak and local meats*	**Presis** *Tapas*
O´Learys *Bar food*	**Arctandria** *Seafood*	**Kitchen and Table** *Variety restaurant*

Downtown Center

Map data ©2018 Google

Mathallen *Fine dining, local ingredients*	**Helmersen** *Deli and wine*	**Tang´s restaurant** *Chinese food*
Rorbua pub	**Yonas Pizzeria** *Pizza*	**Roast** *Variety restaurant*
Asian Healthy foods *Asian wok*	**Sushi Point** *Sushi*	**Pastafabrikken** *Pasta dishes, pizza*
Steakers *Steak*	**Fiskekompaniet** *Sea food fine dining*	**Milano** *Kabobs and pizza*
Flyt *Bar food, hamburgers*	**Lotus mat og vinhus** *Sushi, Asian food*	**Bardus bistro** *Affordable fine dining/local ingredients*
Burger king *Fast-food hamburgers*	**Indie** *Indian cuisine*	**Smørtorget kafe** *Sandwiches, cakes*

Downtown North



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Peppes pizza *Pizza*	**Skirri** *Northern Norwegian cuisine*	**Kaia** *Variety bistro*
Rå *Sushi*	**Elefant** *Indian cuisine*	**Burgr** *Hamburger restaurant*
Beijing home *Chinese food*	**Cous** *Mediterranean food*	**Shanghai wok** *Chinese food*

SERVICES AND PRACTICAL INFORMATION

ATM:

ATMs can be found at DNB and Sparebank1 Nord-Norge in Grønnegata and Fredrik Langes gate, respectively, about 200 meters from the conference venue.

Currency:

The official currency is Norwegian kroner (NOK). 100 NOK ≈ 10 Euros ≈ 12 USD. Note that cash is getting less common in use in Norway, and almost all services accepts debit/credit cards. Please note that **it is not possible to exchange foreign currency into Norwegian kroner in Tromsø**, this has to be done at Oslo Airport Gardermoen or in your home country. You can, however, withdraw Norwegian currency from an ATM (see above).

Electricity:

Norway uses Northern European electrical standards (50 Hz/220-240 volts), and the standard Euro plug socket with two round prongs so you can use adapter types “C” or “F” (often labelled as a Northern Europe adapter). Make sure to check the voltage labels on your appliances or chargers to see if you need to use just an adapter or a converter/transformer with an adapter.

Internet:

Free wireless internet is available at the conference venue. The meeting room *Skarven* can be used for charging your computer and for more extensive work.

Lunch coupons:

If you decide to join the lunch buffet at the conference venue and have not paid for this during registration, please contact the registration desk which can assist you with this. The lunch buffet costs NOK 295/day.

Nursing room:

Melkerampa is located behind the hotel reception and is reserved as a nursing room. There will be a sofa and a nursing table available, as well as chairs for relaxation.

Lecture rooms:

Plenary sessions will be held in *Margarinfabrikken 1+2+3*, located straight ahead from the entrance of the hotel.

Parallel sessions will be held in *Margarinfabrikken 1, 2 and 3* and in *Arbeidskontoret 1+2.* Arbeidskontoret is located to the right of the elevators when you face Margarinfabrikken.

See also the map over the conference venue.

Poster sessions:

There will be two poster sessions. Poster session 1 (label P1) is on Saturday July 13, whereas poster session 2 (label P2) is on Monday July 15. Poster will be placed in several areas of the hotel:

Posters 1-14: On the walls outside *Margarinfabrikken 1+2+3*
Posters 15-24: On the walls of the meeting room *Skarven*
Posters 25-42: In the meeting room *Prostneset*
Posters 43-58: In the meeting room *Importkompaniet*
Posters 59-74: In the meeting room *Kjøpmannskontoret*
Posters 75-139: In the room *Arbeidskontoret 1+2*

See also the map over the conference venue.

Poster award ceremony:

Poster award winners will be announced after the last plenary lecture on July 17 in Margarinfabrikken 1+2+3.

Poster prizes:

There will be a total of 10 poster prizes. Poster prizes have been generously donated by the following journals:

- ACS Omega (https://pubs.acs.org/journal/acsodf)
- Journal of Physical Chemistry (https://pubs.acs.org/journal/jpcafh)
- Journal of Physical Chemistry Letters (https://pubs.acs.org/journal/jpclcd)
- Journal of Chemical Theory and Computation (https://pubs.acs.org/journal/jctcce)
- International Journal of Quantum Chemistry (https://onlinelibrary.wiley.com/journal/1097461x)
- Journal of Computational Chemistry (https://onlinelibrary.wiley.com/journal/1096987x)
- Physical Chemistry Chemical Physics (https://pubs.rsc.org/en/journals/journal/CP)
- Advances in Quantum Chemistry (https://www.sciencedirect.com/bookseries/advances-in-quantum-chemistry)

Registration desk:

The registration desk is located just to the right after the entrance to the hotel. The registration desk will be open:

July 11: 12.30-18.45
July 12: 08.00-18.45
July 13: 08.00-18.45

From July 14 and after these opening hours, please register at the hotel front desk.

Relaxation room:

Skarven will have some chairs/sofas for relaxation.

Skybar:

The Skybar at Clarion Hotel The Edge is located on the 11th floor and allows for great views of the city and the surrounding mountains.

CLARION HOTEL THE EDGE, TROMSØ
BY NORDIC CHOICE

Skala ca. 1:400

Thursday, July 11

17:00	**Opening ceremony** *Room: Margarinfabrikken 1+2+3*
	Plenary lectures *Room: Margarinfabrikken 1+2+3* **Chair: F. Jensen**
17:30	**Sharon Hammes-Schiffer** *Multicomponent Quantum Chemistry: Integrating Electronic and Nuclear Quantum Effects*
18:15	**Trygve Helgaker** *Egil Hylleraas — A Pioneer of Computational Quantum Mechanics*
19:00	**Welcome reception** *Room: Margarinfabrikken 1+2+3*

Friday, July 12

	Plenary lectures *Room: Margarinfabrikken 1+2+3* **Chair: P. Szalay**			
8:30	**Peter Schwerdtfeger** *The Year of the Periodic Table - Going Superheavy*			
9:15	**Sylvio Canuto** *Environment Contribution to Molecular Spectroscopy, Reactivity and Photochemistry*			
	Large-scale electronic structure models of materials *Room: Margarinfabrikken 1* **Chair: T. Heine**	**Machine learning and data-driven approaches in chemical physics** *Room: Margarinfabrikken 2* **Chair: A. Aspuru-Guzik**	**Multiscale modeling including focussed models** *Room: Margarinfabrikken 3* **Chair: B. Mennucci**	**Aspect of Heavy-Element Chemistry** *Room: Arbeidskontoret* **Chair: T. Saue**
10:30	**Ilaria Ciofini** *Modeling Photo-Responsive systems using combined classical and DFT approaches*	**Pavlo Dral** *Quantum Chemistry Assisted by Machine Learning*	**Oleg Prezhdo** *Time-Domain Modeling of Excited State Dynamics in Halide Perovskites*	**Thomas Albrecht-Schmitt** *An Unexpected Route to the Formation of Covalent Bonds in Cerium and Berkelium Coordination Complexes*
11:00	**Shuhua Li** *Generalized energy-based fragmentation approach for large molecules and condensed phase systems*	**Cecilia Clementi** *Machine Learning Models for Biomolecular Dynamics*	**Damien Laage** *Water at electrified graphene interfaces: structure, dynamics, vibrational SFG spectroscopy and consequences for electron transfer reactions*	**Katharina Boguslawski** *Simplified Coupled Cluster Methods for f0 Actinide Compounds*
11:30	**Petko Petkov** *Computational modeling of H/H+ migration in porous and layered materials*	**Marivi Fernandez-Serra** *Machine learning a highly accurate exchange and correlation functional of the electronic density*	**Dominika Zgid** *Finite temperature Green's function theories for periodic systems*	**Han-Shi Hu** *Bonding Pattern Change Induced by Relativistic Effects*
12:00	**Jianping Xiao** *Toward Computational Design of Catalysts for CO2 Selective Reduction via Reaction Phase Diagram Analysis*	**Koji Tsuda** *Expanding the horizon of automated metamaterials discovery via quantum annealing*	**Thomas Markland** *Accurate and Efficient Non-adiabatic Quantum Dynamics using Master Equations*	**Michael Patzschke** *Combined computational and spectroscopical analysis of tetravalent f-element complexes*
	Molecular properties and interactions *Room: Margarinfabrikken 1+2* **Chair: A. Rizzo**	**Multiscale modeling including focussed models** *Room: Margarinfabrikken 3* **Chair: S. Höfener**	**Aspect of Heavy-Element Chemistry** *Room: Arbeidskontoret* **Chair: R. Berger**	
14:00	**Alston Misquitta** *Can we derive many-body non-additive polarization energies from 1-body properties and 2-body energies only?*	**Filippo Lipparini** *A general linear scaling implementation for polarizable embedding methods*	**Luuk Visscher** *Relativistic coupled cluster for a new generation of supercomputers*	
14:30	**Krzystof Szalewicz** *From molecular properties to intermolecular interaction potentials*	**Jean-Philip Piquemal** *Scalable polarizable molecular dynamics using Tinker-HP*	**Andre Severo Pereira Gomes** *Relativistic equation of motion coupled cluster based on four-compoment Hamiltonians*	
15:00	**Andreas Hesselmann** *Intermolecular interaction energies from fourth order many-body perturbation theory. Impact of individual electron correlation contributions*	**Debashree Ghosh** *Photo-processes in biological systems – Need for hybrid QM/MM with polarization*	**Hiromi Nakai** *Relativistic density functional theory with picture-change corrected electron density*	
15:30	**Malgorzata M. Szczesniak** *New Meta-GGA "Workhorses" in Transition Metal Chemistry and SAPT*	**Ksenia Bravaya** *Simulating Electron Transfer in Biomolecules: the Role of Polarization and Long-range Electrostatic Interactions*	**Florian Weigend** *NMR Shielding Tensors and Shifts in the Local Exact Two-Component Theory*	
	Emergent electronic structure methods *Room: Margarinfabrikken 1+2* **Chair: G. Scuseria**	**Path-integral methods** *Room: Margarinfabrikken 3* **Chair: F. Paesani**	**90 years of r12: Hylleraas symposium** *Room: Arbeidskontoret* **Chair: W. Klopper**	
16:30	**Ali Alavi** *Non-unitary Quantum Chemistry*	**David Ceperley** *Melting of the 2D Wigner Crystal*	**Edit Matyus** *Ultra-precise computations for molecular paradigms*	
17:00	**Cyrus Umrigar** *Semistochastic Heatbath Configuration Interaction Method and Orbital Optimization*	**Mark Tuckerman** *A path-integral sampling (trajectory-free) approach to the calculation of quantum time correlation functions*	**Kirk Peterson** *On the Development of Accurate Gaussian Basis Sets for f-Block Elements - Initial Efforts for F12 Correlation Consistent Basis Sets for Uranium*	
17:30	**Eric Neuscamman** *Variational Excited States in DFT, QMC, and Quantum Chemistry*	**Jian Liu** *Path integral Liouville dynamics & a unified framework for path integral molecular dynamics*	**David Tew** *Principal Domains in Local Correlation Theory*	
18:00	**Sandeep Sharma** *Polynomial scaling multireference methods*	**Nancy Makri** *Modular Quantum and Rigorous Quantum-Classical Real-Time Path Integral Methods*	**Hans-Joachim Werner** *Explicitly correlated local coupled-cluster methods for large molecules*	

Saturday, July 13	**Plenary lectures** *Room: Margarinfabrikken 1+2+3* **Chair: P. Surjan**			
8:30	**Peter Gill** *Q-MP2-OS: A new approach to correlation using quadrature*			
9:15	**Peter Saalfrank** *Molecules driven by light: Electron and nuclear dynamics*			
	Physical organic chemistry and catalysis *Room: Margarinfabrikken 1* **Chair: V. Jensen**	**Machine learning and data-driven approaches in chemical physics** *Room: Margarinfabrikken 2* **Chair: C. Clementi**	**From picoseconds to attoseconds: Nuclear and electron dynamics** *Room: Margarinfabrikken 3* **Chair: D. Clary**	**Aspect of Heavy-Element Chemistry** *Room: Arbeidskontoret* **Chair: W. Liu**
10:30	**Robert Paton** *New Mechanisms and Concepts for Organic Reactivity and Enantioselectivity From Computations*	**Olexandr Isayev** *Neural networks learning quantum chemistry*	**Todd J. Martinez** *Potential Energy Surfaces and Nonadiabatic Dynamics in Photoactive Proteins from First Principles*	**Stefaan Cottenier** *Po-containing molecules in fission and fusion reactors*
11:00	**Kathrin Hopmann** *Is Your Mechanism Correct? Insights into Hydrogenation and Carboxylation Reactions*	**Johannes Hachmann** *A Machine Learning Shortcut to Physics-Based Modeling and Simulations*	**Regina de Vivie-Riedle** *Photostability of Uracil affected by RNA environment or shaped light*	**Helene Bolvin** *Magnetic coupling between f centers from first principles*
11:30	**Per-Ola Norrby** *Selectivity models for chemical synthesis*	**Alexandre Tkatchenko** *Towards Exact Molecular Dynamics Simulations with Quantum Chemistry and Machine Learning*	**Leticia Gonzalez** *Excited state dynamics of transition metal complexes using efficient trajectory surface hopping methods*	**Juha Vaara** *Computations of Small Physical Effects in Nuclear Magnetic Resonance*
12:00	**Benedetta Mennucci** *The protein is the key: the unique chemistry of biological pigments revealed by a multiscale strategy*	**Volker Deringer** *From Machine-Learning Interatomic Potentials to Atomic-Scale Materials Science*	**Graham Worth** *Simulating Non-adiabatic Photochemistry using Grids and Gaussians*	**Michal Jaszunski** *Nuclear magnetic dipole moments from NMR experiments*
	ERC session *Room: Margarinfabrikken 2*			
12:45-13:45	**Daniele Mammoli (ERC)** *European Research Council session*			
	90 years of r12: Hylleraas symposium *Room: Margarinfabrikken 1* **Chair: T. Helgaker**	**Molecular properties and interactions** *Room: Margarinfabrikken 2* **Chair: D. Wilson**	**Path-integral methods** *Room: Margarinfabrikken 3* **Chair: T. Miller**	
14:00	**Angela Wilson** *Resolution-of-the-Identity and Beyond*	**Katharine Hunt** *New ab initio results for interaction-induced dipoles and susceptibilities and new analytical results for transition probabilities*	**Stuart Althorpe** *Real-time dynamics from imaginary-time path-integrals: theory and practice*	
14:30	**Florian Bischoff** *Explicitly Correlated Coupled-Cluster in Real Space*	**Jacob Kongsted** *Polarizable Density Embedding for Proteins: Excited States in Complex Environments*	**David Manolopoulos** *Path integral methods for reaction rates*	
15:00	**Andreas Grüneis** *Recent progress in applying periodic coupled cluster theory to solids and surfaces*	**Toon Verstraelen** *Modeling Weak Interactions With Spherical Atomic Electron Densities*	**Joseph Lawrence** *On the calculation of quantum mechanical electron transfer rates*	
15:30	**Andreas Köhn** *Computing molecular properties in multireference coupled-cluster theory*	**Denis Jacquemin** *Searching for Super-Accuracy in Excited State Calculations*	**Jeremy Richardson** *Nonadiabatic quantum transition-state theory*	
	Aspect of Heavy-Element Chemistry *Room: Margarinfabrikken 1* **Chair: P. Pyykkö**	**Emergent electronic structure methods** *Room: Margarinfabrikken 2* **Chair: A. Szabados**	**Multiscale modeling including focussed models** *Room: Margarinfabrikken 3* **Chair: L. Slipchenko**	
16:30	**Aurora Clark** *Heavy Element Solution Chemistry – A Sojourn Through Ideal and Non-Ideal Solutions and Their Interfaces*	**Piotr Piecuch** *Toward Exact Quantum Chemistry by a Combination of Stochastic Wave Function Sampling and Deterministic Coupled-Cluster Computations*	**Aurelien de la Lande** *Toward First Principles Simulations of Biological Matter under Ionizing Radiations*	
17:00	**Jochen Autschbach** *Chemical bonding, core spectroscopy, and magnetic properties of actinide complexes*	**Gustavo Scuseria** *Quantum Chemistry for Strong Correlation*	**Joachim Sauer** *Ab initio Free Energy Calculations with Chemical Accuracy for Molecule - Surface Interactions*	
17:30	**Xiaosong Li** *Spin-Orbit Symmetry Breaking and Restoring in Kramers-Unrestricted Multireference Approaches*	**Paola Gori-Giorgi** *Strong-coupling limit in DFT and Hartree-Fock: kinetic correlation energy and dispersion*	**Chao-Ping Hsu** *Machine learning for electron-transfer couplings*	
18:00	**Michal Repisky** *All-electron relativistic four-component Dirac–Kohn–Sham theory for solids using Gaussian-type functions*	**Laura Gagliardi** *Multireference Methods for Extended Systems*	**Rosa Bulo** *Multi-scale Modeling of Chemistry in Water*	
19:00	**Poster session 1**			

Sunday, July 14	**Machine learning and data-driven approaches in chemical physics** *Room: Margarinfabrikken 1+2* **Chair: P. Dral**	**Molecular properties and interactions** *Room: Margarinfabrikken 3* **Chair: G. Chalasinski**	**Computational biophysics** *Room: Arbeidskontoret* **Chair: M. Ramos**
8:30	**Şule Atahan-Evrenk** *Prediction of Intramolecular Reorganization Energy Using Machine Learning*	**Berta Fernandez** *Pursuing accuracy in intermolecular potentials and spectra*	**Helmut Grubmüller** *Atomistic Simulation of Biomolecular Function: Ribosomal Translation, Ligand Binding Heterogeneity, and a Dynasome Perspective*
9:00	**Thomas Heine** *Challenges for automated materials discovery*	**Patrick Norman** *VeloxChem: an efficient implementation of real and complex response functions at the level of Kohn–Sham density functional theory*	**Nathalie Reuter** *Interfacial choline-aromatic cation-pi interactions can contribute as much to peripheral protein affinity for membranes as aromatics inserted below the phosphates*
9:30	**Alan Aspuru-Guzik** *The Materials for Tomorrow, Today*	**Sonia Coriani** *Molecular Properties and Interactions: A Wonderful Playground for a Theoretical Chemist*	**Teresa Head-Gordon** *How to Make an Enzyme: Computational Optimization of Electric Fields for Better Catalysis Design*

Sunday, July 14	**Computational spectroscopy: from X-rays to microwaves** *Room: Margarinfabrikken 1+2* **Chair: H. Ågren**	**Path-integral methods** *Room: Margarinfabrikken 3* **Chair: T. Markland**	**90 years of r12: Hylleraas symposium** *Room: Arbeidskontoret* **Chair: M. Hoffman**
10:30	**Shaul Mukamel** *Ultrafast spectroscopy and imaging of molecules with classical, quantum, and noisy x-ray pulses*	**Angelos Michaelides** *Towards an improved understanding of interfacial water*	**Anna-Sophia Hehn** *Explicitly correlated wave function approaches based on the random phase approximation*
11:00	**Malgorzata Biczysko** *From spectroscopic signatures to 3-D structure of protein building blocks*	**Mariana Rossi** *Anharmonic Nuclear Quantum Effects and their Interplay with the Electronic Structure of Weakly Bonded Systems*	**Seiichiro L. Ten-no** *Explicitly correlated F12 theory on modern electronic structure calculations*
11:30	**Jonathan Tennyson** *The ExoMol project: molecular line lists for the opacity of exoplanets and other hot atmospheres*	**Michele Ceriotti** *Efficient Modeling of Thermal and Quantum Fluctuations in Materials and Molecules*	**Jan M. L. Martin** *Do CCSD and Approximate CCSD-F12 Variants Converge to the Same Basis Set Limits? The Case of Atomization Energies*
12:00	**Elke Fasshauer** *Time-Resolved Measurement of Interparticle Coulombic Decay Processes*	**Francesco Paesani** *Nuclear Quantum Effects in Ion-Mediated Hydrogen-Bond Rearrangements*	**Ludwik Adamowicz** *Quantum-mechanical non-Born-Oppenheimer calculations of small atoms and molecules*

Monday, July 15	**Plenary lectures** *Room: Margarinfabrikken 1+2+3* **Chair: R. Broer**			
8:30	**Thomas F. Miller** *Classical and Machine-Learning Methods for Quantum Simulation*			
9:15	**Irene Burghardt** *High-Dimensional Quantum Dynamics of Functional Organic Polymer Materials: Coherence, Confinement, and Disorder*			
	Large-scale electronic structure models of materials *Room: Margarinfabrikken 1* **Chair: D. Fedorov**	**Emergent electronic structure methods** *Room: Margarinfabrikken 2* **Chair: J. Pittner**	**Molecular properties and interactions** *Room: Margarinfabrikken 3* **Chair: K. Szalewicz**	**Computational biophysics** *Room: Arbeidskontoret* **Chair: P. Imhof**
10:30	**Volker Blum** *Accurate, Scalable All-Electron Theory Across the Periodic Table: Organics, Inorganics, Hybrids*	**Claudia Filippi** *The force awakens in quantum Monte Carlo*	**Stefan Grimme** *New Tight-Binding Quantum Chemistry Methods for the Exploration of Chemical Space*	**Madhurima Jana** *Stability of Proteins in Solutions: A Microscopic Investigation on the Role of Surrounding Water/Cosolvent*
11:00	**Christian Ochsenfeld** *Quantum-chemical methods for biochemical systems*	**Brenda Rubenstein** *Ab Initio Finite Temperature Auxiliary Field Quantum Monte Carlo for Solids*	**Lyudmila Slipchenko** *Polarizable embedding for biological systems: Modeling photoactive proteins with the Effective Fragment Potential method*	**Michele Cascella** *Simulating Biological Systems Coupling Particles and Fields with Molecular Dynamics*
11:30	**Joost VandeVondele** *Linear scaling DFT accelerated with GPUs and ML*	**Fabien Bruneval** *The linearized GW density matrix*	**Attila Csaszar** *Quasistructural molecules*	**Mikko Karttunen** *Computational modelling of cellulose and its modifications*
12:00	**Steven G. Louie** *Many-electron Correlations in Multi-particle Excitations and Nonlinear Optical Processes in Materials*	**Katarzyna Pernal** *Dynamic Correlation for CASSCF Reference with Adiabatic Connection Approaches: Open Shell Systems and Dispersion Interaction*	**Tatiana Korona** *On the Applicability of Various Partitioning Schemes to Intermolecular Interactions*	**Monika Fuxreiter** *Conformational heterogeneity in enzymatic catalysis and evolution*
	Physical organic chemistry and catalysis *Room: Margarinfabrikken 1* **Chair: M. Podewitz**	**From picoseconds to attoseconds: Nuclear and electron dynamics** *Room: Margarinfabrikken 2* **Chair: L. Gonzalez**	**Ultracold chemical physics** *Room: Margarinfabrikken 3* **Chair: B. Jeziorski**	
14:00	**Satoshi Maeda** *Systematic Generation and Analysis of Reaction Path Networks by the Artificial Force Induced Reaction Method*	**Fernando Martin** *Attosecond pump-probe spectroscopy of molecular electron dynamics*	**Guido Pupillo** *Cavity-induced collective dissipation for cold chemistry*	
14:30	**Natalie Fey** *CatLab – Putting calculation before experiment in organometallic catalysis*	**Eberhard Gross** *Potential energy surfaces and Berry phases from the exact factorization: A rigorous approach to non-adiabatic dynamics*	**Olivier Dulieu** *Ultracold doubly-polar molecules: on the way to create them via a Laser-Assisted Self-Induced Feshbach Resonance*	
15:00	**Markus Reiher** *Quantum Chemical Exploration of Catalytic Reaction Networks*	**Nina Rohringer** *Stimulated X-Ray Emission Spectroscopy for Chemical Analysis*	**Robert Moszynski** *New physics with ultracold strontium molecules*	
15:30	**Heather J. Kulik** *Transition metal catalyst discovery with high-throughput screening and machine learning*	**Boutheina Kerkeni** *Understanding H2 Formation on hydroxylated nanopyroxene clusters: Ab initio Study of the Reaction Energetics and Kinetics*	**Svetlana Kotochigova** *Nonadiabatic Transitions via Conical Intersections in Ultracold Chemical Reactions*	
	Computational spectroscopy: from X-rays to microwaves *Room: Margarinfabrikken 1* **Chair: B. Durbeej**	**Emergent electronic structure methods** *Room: Margarinfabrikken 2* **Chair: S. Goedecker**	**Path-integral methods** *Room: Margarinfabrikken 3* **Chair: D. Manolopoulos**	
16:30	**Julien Bloino** *A Virtual Spectrometer to Predict and Interpret Vibrational Spectra*	**Steven R. White** *Multisliced Gausslet Bases for Electronic Structure*	**Barak Hirshberg** *Path Integral Molecular Dynamics for Bosons*	
17:00	**Tucker Carrington** *Collocation methods for computing vibrational spectra*	**Garnet Chan** *Progress in quantum embedding in the condensed phase*	**Seogjoo Jang** *Quantum Fokker-Planck equation with positive definiteness condition via path integral influence functional formalism*	
17:30	**Ad van der Avoird** *Spectra of O2 induced by collisions with N2 and O2*	**Philippe Corboz** *Simulation of strongly correlated systems with 2D tensor networks*	**Pierre-Nicholas Roy** *Quantum dynamics of confined molecules*	
18:00	**Fabien Gatti** *The polyspherical approach: recent applications to spectroscopy*	**Örs Legeza** *Attosecond electron dynamics via tensor network state methods in strongly correlated molecular systems*	**Gregory A. Voth** *Coarse-graining of Feynman Path Integrals in Statistical Mechanics*	
19:00	**Poster session 2**			

Tuesday, July 16				
	Plenary lectures *Room: Margarinfabrikken 1+2+3* **Chair: D. Crawford**			
8:30	**Giulia Galli** *Simulating energy conversion processes from first principles*			
9:15	**Zhigang Shuai** *Density matrix renormalization group: time-dependent formalism, light-emitting, carrier transport, and singlet fission*			
	Physical organic chemistry and catalysis *Room: Margarinfabrikken 1* **Chair: O. Eisenstein**	**Large-scale electronic structure models of materials** *Room: Margarinfabrikken 2* **Chair: M. Mayes**	**Ultracold chemical physics** *Room: Margarinfabrikken 3* **Chair: J. Hutson**	**Janos Ladik memorial symposium** *Room: Arbeidskontoret* **Chair: A. Bende**
10:30	**Yousung Jung** *Catalysts Discovery and Understanding with Computational and Data-Driven Approaches*	**Helio A. Duarte** *Unveiling the chemical reactivity of sulfide mineral surfaces in the presence of water and oxygen*	**Paul Julienne** *Calculations of three body recombination and dimer product distributions from ultracold atomic collisions*	**Rodney J. Bartlett** *The devil's triangle in KS-DFT calculations and how to fix it*
11:00	**Carine Michel** *Modeling reactivity at the catalyst/water interface*	**Johannes Neugebauer** *Exact Subsystem Time-Dependent Density-Functional Theory*	**John Bohn** *Ultracold Collisions of Polyatomic CaOH Molecules*	**Alia Tadjer** *Molecular modelling of hybrid-ion batteries*
11:30	**Hai Lin** *Simulations of Ion Solvation and Transfer by Adaptive-Partitioning QM/MM Dynamics*	**Marcus Elstner** *Multi-scale methods for electron and exciton transfer in biological and organic materials*	**Robin Cote** *Optical production of polyatomic complex in ultracold regime*	**Martin Quack** *Fundamental and approximate symmetries, parity violation and tunnelling in chiral and achiral molecules*
12:00	**Michelle Coote** *Catalyzing and Controlling Chemical Reactions with Electric Fields*	**Tsuyoshi Miyazaki** *Linear-scaling DFT simulations of complex nano-structured materials using the CONQUEST code*	**Tijs Karman** *Collisional loss of ultracold molecules*	**Cleanthes Nicolaides** *Attosecond-resolved Quantum Chemistry. Predictions from the early years and comparison with recent experiments*
	Emergent electronic structure methods *Room: Margarinfabrikken 1+2* **Chair: C. Hättig**	**Computational spectroscopy: from X-rays to microwaves** *Room: Margarinfabrikken 3* **Chair: V. Liegeois**	**Computational biophysics** *Room: Arbeidskontoret* **Chair: B. Brandsdal**	
14:00	**Michiel van Setten** *Benchmarking GW for quantum chemistry applications*	**Faris Gelmukhanov** *X-ray Raman scattering of liquids*	**Inaki Tunon** *Quantum Hydride Transfer in Formate Dehydrogenase: Environment Reorganization and Primary and Secondary Hydrogen Motions*	
14:30	**Stefan Goedecker** *Wavelets for electronic structure calculations, an introduction and overview*	**Vincenzo Carravetta** *Aqueous solutions: a look at the surface*	**Maria Joao Ramos** *Understanding enzymatic reactions*	
15:00	**Luigi Genovese** *Potentialities of Wavelet formalisms for large-scale DFT calculations and beyond*	**Barbara Brena** *Calculation of X-Ray Absorption and Photoemission Spectra of Molecules in Complex Environment*	**Qiang Cui** *QM/MM analysis of metalloenzymes: developments and applications*	
15:30	**Luca Frediani** *MRChem: Quantum Chemistry at the basis set limit with Multiwavelets*	**Weijie Hua** *Computational optical and X-ray spectroscopy studies for crystals & 2D materials*	**Fernanda Duarte Gonzalez** *Unraveling the Role of Non–Covalent Interactions in Recognition and Catalysis*	
	Large-scale electronic structure models of materials *Room: Margarinfabrikken 2* **Chair: H. Nakai**	**From picoseconds to attoseconds: Nuclear and electron dynamics** *Room: Margarinfabrikken 3* **Chair: F. Martin**	**Ultracold chemical physics** *Room: Arbeidskontoret* **Chair: P. Julienne**	
16:30	**Woo Youn Kim** *Efficient hybrid density functional calculations in real-space numerical grid methods*	**David Clary** *Quantum Tunnelling in Chemical Reactions*	**Rosario Gonzalez-Ferez** *Rydberg polyatomic molecules: Electronic structure and experimental proposal for their creation*	
17:00	**Beatriz Gonzalez del Rio** *Large-scale Ab Initio Simulations with Orbital-free Density Functional Theory*	**Francoise Remacle** *Spatial and temporal localization of the vibronic and photoelectron wave packets in LiH photoexcited by intense few cycle IR pulses*	**Timur Tscherbul** *Magnetic tuning of ultracold chemical reactions: Theoretical insights*	
17:30	**Damiano Marian** *Multi-scale approach: a versatile platform for investigating novel two-dimensional-material based device concepts*	**Olga Smirnova** *Synthetic chiral light for extremely efficient laser-controlled chiral discrimination*	**Christiane Koch** *Quantum effects in cold and controlled molecular dynamics*	
18:00	**David Tomanek** *Magic with Semiconducting 2D Nanolayers*	**Morgane Vacher** *Insights into chemiluminescence from molecular dynamics simulations and machine learning analysis*	**Goulven Quemener** *Shielding ultracold molecules against losses in collision*	
20:30	**Conference dinner** *Room: Margarinfabrikken 1+2+3*			

Wednesday, July 17			
	Computational spectroscopy: from X-rays to microwaves *Room: Margarinfabrikken 1+2* **Chair: A. Csaszar**	**Computational biophysics** *Room: Margarinfabrikken 3* **Chair: F. Duarte**	**Janos Ladik memorial symposium** *Room: Arbeidskontoret* **Chair: K. Ruud**
8:30	**Csaba Fabri** *From High-Resolution Spectroscopy to Light-Dressed Molecules*	**Rafael Bernardi** *NAMD as a tool for in silico force spectroscopy*	**Mark Hoffman** *Multireference Configuration Interation Beyond Singles and Doubles*
9:00	**Cristina Puzzarini** *Rotational Spectroscopy Meets Quantum Chemistry for Elucidating Astrochemical Challenges*	**Michele Vendruscolo** *Systematic development of small molecules to inhibit amyloid beta aggregation in Alzheimer's disease*	**Hazel Cox** *The Limits of Stability in Three-Body Coulomb Systems*
9:30	**Sandra Luber** *Recent developments in dynamic spectroscopic methods for the gas and condensed phase*	**Ramon Crehuet** *Stabilization of α-helices by side-chain to main hydrogen bonds. Can current force fields describe the hydrophobic shielding?*	**Samantha Jenkins** *Beyond Scalar Measures: Directional Chemical Perspective with Next Generation QTAIM*
	Plenary lectures *Room: Margarinfabrikken 1+2+3* **Chair: E. Brändas**		
10:30	**Monica Olvera de la Cruz** *Properties of Molecular Electrolytes*		
11:15	**Kersti Hermansson** *OH, ceriously, ... Molecules + materials = difficult!*		

Title: Quantum-mechanical non-Born-Oppenheimer calculations of small atoms and molecules.

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Abstract

In this presentation I will describe the work carried out in my group concerning the development of quantum-mechanical methods for calculating bound states of small atoms and molecules without assuming the Born-Oppenheimer approximation. In the non-BO approach all particles forming the system (nuclei and electrons) are treated on equal footing. The energies of the states, which in the case of atoms include electronic ground and excited states and in the case of molecules include a combination of electronic and rovibrational states, are obtained in variational calculations using various types of all-particles explicitly correlated Gaussian (ECG) functions as basis functions. The wave function and the energy of each state is obtained in a separate calculation where its energy is minimized in terms of the non-linear parameters of the Gaussians. In the minimization, the analytically evaluated energy gradient determined with respect to the parameters is employed. This presentation is particularly focused on our works concerning the selection of ECG basis sets that enable non-BO calculations of atomic and molecular bound states with high accuracy.

Abstract for the ISTCP-X Conference

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We investigate the utility of non-unitary similarity transformations, based on Jastrow or Gutzwiller factorisation of the electronic wavefunction. Such factorisations generally lead to non-Hermitian effective Hamiltonians which contain three-body interactions. Such Hamiltonians are treatable via the projective FCIQMC technique, which does not suffer from the non-Hermitian characteristic of the Hamiltonian, nor do the 3-body terms present an insuperable obstacle. In this formalism, there is no need for projection operators that are essential in R12/F12 type of explicit correlation methods, and highly flexible Jastrow factors can be used. We show that these are effective in delivering highly accurate total enegeries even with modest basis sets. In the case of Gutzwiller factorisation, we apply this method to the 2D Hubbard model in the strong correlation off-half-filling regime, which is an extremely challenging problem. We show that the similarity transformation results in compact right eigenvectors, which can be sampled accurately by the i-FCIQMC method, even for systems containing 50 sites and ~50 electrons. The methodology opens up the prospect to study strongly correlated molecular systems, where much of the dynamical correlation can be captured by the correlation factor, and the strong correlation aspects via the multi-configurational reference function.

An Unexpected Route to the Formation of Covalent Bonds in Cerium and Berkelium Coordination Complexes

Alyssa Gaiser, Cristian Celis-Barros, Frankie White, Joseph Sperling, and Thomas E. Albrecht-Schmitt

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This talk will focus on the unexpected observation of a “plane of covalency” that apparently exists in a family of lanthanide and actinide coordination complexes that possess an unusually polarized ligand. The atypical bonding exhibited by these complexes alters the nature of the ground states of the metal ions from what would typically be observed as evidenced from EPR spectra, magnetic susceptibility measurements, and evaluation of bond distances obtained from low-temperature crystal structures. Theoretical predictions led to the supposition that these effects would be enhanced by extrapolating from Ce^{III} to Bk^{III} with the latter being the closest electrochemical analog of cerium in the actinide series. The berkelium complex was prepared with great difficulty and the theoretical predictions were validated in regard to both expect bond metrics and electrochemical behavior.

Real-time dynamics from imaginary-time path-integrals: theory and practice

George Trenins[a], Michael J. Willatt[b], Timothy J.H. Hele[a] and Stuart C. Althorpe[a]

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Imaginary-time path-integrals or 'ring-polymers' are a long-established practical technique for simulating quantum Boltzmann statistics. More recently, they have also been used to simulate real-time dynamics, using the centroid molecular dynamics (CMD) [1] and (thermostatted) ring-polymer molecular dynamics ((T)RPMD) [2,3] methods. Here, we show that the theoretical basis of CMD and RPMD is a classical dynamics which arises when the exact quantum dynamics is represented using path-integrals and is coarse-grained to make it a smooth and differentiable function of imaginary-time. [4,5,6] This 'Matsubara' dynamics cannot be used as a practical method (because of a severe sign problem), but can be used to critique and refine heuristic methods such as CMD and RPMD, which turn out to be approximations to Matsubara dynamics that avoid the phase. In particular, we will show how to extend quantum simulations of the infrared spectrum of liquid water and ice to lower temperatures (150 K) than hitherto possible.

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The Materials for Tomorrow, Today

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In this talk, I argue that for materials discovery, one needs to go beyond simple computational screening approaches followed by traditional experimentation. I have been working on the design and implementation of what I call “materials acceleration platforms” (MAPs). MAPs are enabled by the confluence of three disparate fields, namely artificial intelligence (AI), high-throughput quantum chemistry (HTQC), and robotics. The integration of prediction, synthesis and characterization in an AI-driven closed-loop approach promises the acceleration of materials discovery by a factor of 10, or even a 100. I will describe our efforts under the Mission Innovation umbrella platform around this topic.

Prediction of Intramolecular Reorganization Energy Using Machine Learning

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Machine learning techniques offer opportunities for accelerated computational design and discovery. Reorganization energy (RE) is one of the important charge transport parameters suitable for molecular level screening for organic semiconductors. To investigate the possibility of prediction of the RE from the molecular structure by means of machine learning methods, we generated a molecular library of 5631 molecules with extended conjugated backbones. We used benzene, thiophene, furan, pyrrole, pyridine, pyridazine and cyclopentadiene as building blocks for the combinatorial generation of the molecule set and obtained the electronic data at the level of B3LYP level of theory with 6-31G* basis. We compared ridge, kernel ridge, and deep neural net (DNN) regression models based on the graph- and geometry-based descriptors and found that DNN could be used to predict the RE with a mean-absolute-error of 6±10 meV. This study showed that the total RE of organic semiconductor molecules could be predicted from the molecular structure to a high accuracy. We also investigated the possibility of the prediction of the individual contributions of the vibrational modes to the relaxation energy upon ionization.

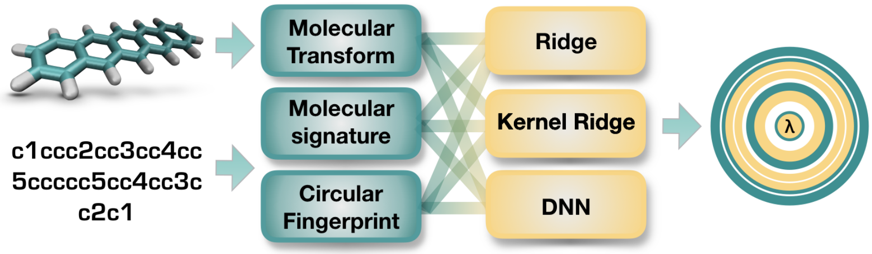

Figure 1: Prediction of the reorganization energy, λ, from molecular structure.

Chemical bonding, core spectroscopy, and magnetic properties of actinide complexes

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Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, magnetic circular dichroism, core excitation spectra, and other types of spectra, of actinide complexes, and how the observed properties relate to the chemical bonding involving the actinide. Of particular interest is the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of the aforementioned magnetic and spectroscopic properties of f-element complexes utilizing relativistic quantum chemical methods.

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Abstract for ISTCP Tromsö, July, 2019.

THE DEVIL'S TRIANGLE IN KS-DFT CALCULATIONS AND HOW TO FIX IT

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Most of the problems with KS-DFT arise from three interconnected failures, self-interaction, the one particle spectrum, and the integer discontinuity. By introducing an eigenvalue ionization potential theorem justified by adiabatic TDDFT, the ground state KS problem has to have all its occupied orbitals tied to eigenvalues that are good approximations to the principal ionization potentials of molecules. When that is achieved then one has the right photo-electron spectrum, which provides meaningful molecular orbitals for a problem. Once that is accomplished, then the KS-DFT method also ameliorates the SI problem. Finally, the integer discontinuity that occurs when adding or removing an electron is mitigated by getting the right IP's and EA's for a problem. The latter turns out to be a by- product of the eigenvalue IP theorem. The above leads to the family of QTP parametrizations of the well-known CAM-B3LYP range separated functional, improving upon it in all respects.

Recent work has addressed the time-dependent coupled-cluster and QTP functional description of core excitation spectra.

Rodney J. Bartlett, Perspective Article, Journal of Chemical Physics, "Adventures in DFT by a Wavefunction Theorist", in press.

Rodney J. Bartlett, Duminda S. Ranasinghe, Frontier Article, "The Power of Exact Conditions in Electronic Structure Theory, " Chemical Physics Letters **669** (2017) 54–70

NAMD as a tool for *in silico* force spectroscopy

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The concept of employing mechanical forces to shape macroscopic materials can be considered of universal knowledge. The outcome of applying mechanical forces into to a material is recognizably dependent on the direction of the force application. For instance, a transverse force can easily bend an iron bar, while a much higher longitudinal force is needed to deform it. A far more intriguing question is how mechanical forces affect single biomolecules. In fact, the chemistry at high forces can be really surprising. Recently, we have shown that an array of hydrogen bonds can be as strong as a covalent bond when a macromolecular system is designed such that all hydrogen bonds must be broken at the same time to separate a protein-peptide complex [1]. Nevertheless, if force is applied in an unfavorable geometry, the protein complex can become relatively weak. Indeed, the directionality of force loading can regulate key biological activities. For instance, some genetic diseases are associated to single mutations in mechanoactive proteins. This mutations affect how these proteins behave under force load, causing significant phenotypic differences in humans. Still, studying different force-loading geometries on the single-molecule level is not straightforward and little is known about how protein complexes behave under mechanical load [2]. Experimentally, modern force spectroscopy investigates these issues by taking advantage of atomic force microscopes, and of both magnetic and optical tweezers. In my talk I will show how, boosted by a GPU-accelerated NAMD [3], we are employing a wide-sampling approach on molecular dynamics simulations to acquire atomistic details to these experimental approaches. Steered molecular dynamics simulations, when carefully performed and combined with single-molecule atomic force spectroscopy experiments, can predict and explain the behavior of highly mechanostable protein complexes [4]. A great example of highly mechanostable protein complexes is found in the adhesion mechanism of staphylococcal bacteria to its human host. Our joint computational-experimental approach revealed not only how strong this protein complex is, but also the molecular details that are responsible for such strength [1]. The mechanism proposed provides an atomistic understanding of why these adhesins can adhere to their hosts so resiliently, from which possible routes to inhibit it and impede staphylococcal adhesion may be derived.

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From spectroscopic signatures to 3-D structure of protein building blocks

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A comprehensive analysis of the properties of amino acids oligomers and the detailed characterization of their supra-molecular structure, orientation and dynamics is the basic requirement for understanding the structure-function relationships. Molecular structures can be "directly" obtained from microwave (MW) spectroscopy (amino acids and small peptides) or X-ray crystallography and cryo-EM (proteins). On the other hand, structure and properties can be monitored by different spectroscopic measurements such as infrared (IR), Raman, Resonance Raman, UV-vis absorption or fluorescence or circular dichroism (CD), electron spin resonance (ESR). However, it is seldom straightforward to link directly the experimental data to the desired information on the specific structure and properties of complex molecular systems. Moreover, traditionally, these experimental results are analysed separately. Quantum chemistry computations provides a missing link between different experimental techniques, which could not be integrated and fully explored otherwise.

I will discuss status and perspective of the project aimed at spectroscopy studies for systems of increasing size and complexity, from small prebiotic molecules to large bio-molecules, complexes and oligomers. We devise effective theoretical schemes through step-by-step strategy, starting from comparison with highly accurate theoretical models and/or state-of-the art experimental data for isolated amino acids and small peptides, gradually moving towards larger and more complex molecular systems featuring dispersion interactions, hydrogen bonding, variable local stereochemistry-conformation, and chirality.

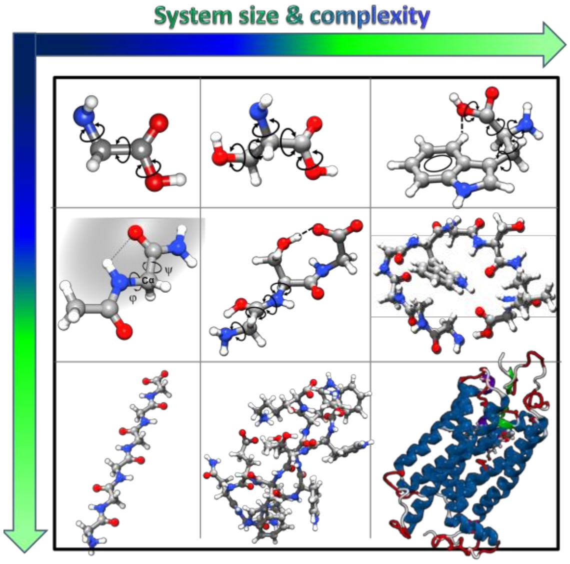

Figure 1: Step-by-step derivation and validation of computational models, from small prebiotic molecules to larger bio-molecules, complexes and oligomers.

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Explicitly Correlated Coupled-Cluster in Real Space

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A first-quantized formulation of Coupled-Cluster is presented and used to implement Coupled-Cluster in real-space methods. All terms that are usually derived in diagrammatic form and are then transferred to second quantization, can be expressed in first quantization. The full regularization of all singularities using explicit correlation makes the method feasible. An implementation of CC2 using multi-resolution analysis (MRA) in the `Madness` program packages shows its applicability for small molecules, and correlation energies close to the basis set limit are obtained. Furthermore, CC2 excitation energies are computed using the same regularization procedure as for the ground state.

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A Virtual Spectrometer to Predict and Interpret Vibrational Spectra

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Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experiment, providing insights of the underlying elementary phenomena responsible for the overall band-shape. However, the reliability of the produced results is strongly correlated to the underlying models. This aspect can be especially critical in some fields of applications like chiroptical analysis or astrochemistry, for instance. Such considerations emphasize the need of carefully setting up computational protocols, in particular by selecting the most appropriate level of theory available. As a matter of fact, for medium-to-large molecular systems with possible environmental effects, a trade-off is necessary between accuracy and computational cost, and several strategies can be devised, with suitabilities varying depending on the cases.

To facilitate the setup of the most efficient and reliable route for the simulation of accurate spectra, we have been developing a versatile and modular platform, called virtual spectrometer [1,2]. In this contribution, we will illustrate the possibilities offered by such a tool as a versatile companion to experiment, with emphasis on vibrational spectroscopy. Thanks to modern processing powers, the systematic or tailored inclusion of anharmonic contributions, even for medium-to-large molecules, has become possible. Despite their undeniable worth[3-5], the inherent complexity of anharmonic models, coupled to their sensitivity to the underlying electronic structure calculations, represents a serious hurdle to a broader application. Focusing on the second-order vibrational perturbation theory (VPT2)[6], we will present some of its pitfalls and highlight how robust protocols can be designed and automatized to build friendlier tools requiring minimal input from the user.[2] Finally, by choosing a suitable representation, intermediate data produced during simulations can be exploited to assess the reliability of the results and provide further insights into the origin of the observed signal.[7]

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Accurate, Scalable All-Electron Theory Across the Periodic Table: Organics, Inorganics, Hybrids

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This talk summarizes recent progress towards accurate, scalable all-electron theory of materials and molecules on equal footing in a framework based on numerically tabulated, atom-centered orbital basis functions, the FHI-aims code [1]. The primary production method is density-functional theory (DFT, semilocal and hybrid) as well as many-body perturbation theory such as GW, the random-phase approximation, the Bethe-Salpeter Equation, and others. Seamless scalability up to thousands of atoms (non-periodic and periodic) is guaranteed by the open-source "ELSI" infrastructure [2], a general-purpose interface for massively parallel (generalized) Kohn-Sham solutions using traditional $\mathrm{O}(\mathrm{N}^3)$ or better-scaling solvers, now used by several different electronic structure codes. We also touch upon recent work on benchmarking different approaches to spin-orbit coupling [3] and on a GPU implementation of key algorithms for (currently) semilocal density functional theory with significant speed-ups over multicore execution on the CPU part of a node. A key strength of the code is its ability to carry out hybrid DFT calculations [4] including spin-orbit coupling for periodic system sizes above thousand atoms without any significant approximations to the potential shape or basis set accuracy. This is particularly relevant in recent work on large, crystalline layered organic-inorganic hybrid perovskites, an emerging class of semiconductors that are tunable by leveraging the arsenal of synthetic organic chemistry and now subject to attention by a very large community. We demonstrate this tunability for several examples of lead-based [5] and lead-free [6] organic-inorganic hybrids, showing how computational predictions can facilitate effective candidate material selection for experimental synthesis [7].

The methodological work reported in this talk would not be possible without the continued support and contributions from the very large community of developers and users of the FHI-aims code, as well as the community around the ELSI infrastructure. The work on perovskites leans heavily on close collaborations with leading experimental colleagues, particularly the group of David Mitzi (Duke University).

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DOI: 10.1039/C9MH00366E

Simplified Coupled Cluster Methods for f0 Actinide Compounds

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Heavy-element-containing compounds are immensely difficult to model theoretically because both correlation effects and relativistic effects have to be described on equal footing, which poses a challenge for present-day quantum chemistry, especially when the molecule under study contains more than one heavy element. As scalar relativistic effects are nowadays relatively straightforward to treat and there are sufficiently accurate approaches to treat spin-orbit interactions perturbatively, the remaining difficulty in computational heavy element chemistry is the large number of degenerate or quasi-degenerate orbitals, which requires a multi-reference treatment. However, present-day quantum chemistry lacks simple, robust, efficient, and cheap algorithms for a qualitatively correct description of strongly-correlated electrons encountered, for instance, during bond-breaking processes as well as in transition metal and actinide chemistry.

We present a conceptually different approach that is well suited for strongly-correlated electrons, but does not use the orbital model. Our method exploits the feature that electron correlation effects can be built into the many-electron wavefunction using two-electron functions, also called geminals. One of the simplest, practical geminal approaches is the Antisymmetric Product of 1-reference-orbital Geminals (AP1roG) [1-3], which is equivalent to the pair-Coupled-Cluster Doubles model [4].

In this work, we discuss the performance of AP1roG-based methods [3,5] in modeling electronic structures for molecules containing heavy elements, including actinides [1-3,5]. We will present different excited state models [6-8] that allow us to target singly- and doubly-excited states with electron-pair theories. Our study indicates that geminal-based approaches provide a cheap, robust, and accurate alternative for the description of electron correlation effects in both ground and excited states.

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Ultracold Collisions of Polyatomic CaOH Molecules

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Ultracold collisions of the polyatomic species CaOH are considered, in internal states where the collisions should be dominated by long-range dipole-dipole interactions. The computed rate constants suggest that evaporative cooling can be quite efficient for these species, provided they start at temperatures achievable by laser cooling. The rate constants are shown to become more favorable for evaporative cooling as the electric field increases. Moreover, long-range, weakly-bound dimer states $(CaOH)_2$ are predicated to occur, having lifetimes on the order of microseconds.

Lecture: Lec-15

Magnetic coupling between f centers from first principles.

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The field of molecular magnetism explores more and more molecules containing lanthanide or actinide atoms. The large spin-orbit coupling and the semi-core character of the 4f and 5f orbitals confer to these molecules novel magnetic properties. Since a decade, there has been a large investigation of complexes with one magnetic center and first principles calculations have become an essential tool to interpret the experimental data, providing the nature of the ground state, the energy of exciting states and the corresponding directions of the magnetic moments.

The next experimental challenge is to gather several magnetic centers in a rational way in order to get a synergetic building of the local bricks. To achieve that, a fine knowledge of the magnetic interaction between centers is necessary. Due the semi-core character of the magnetic orbitals, the magnetic coupling between two f centers is very small, and the mechanism is still in question. The aim of this presentation is to show that quantum chemistry brings physical insights for the analysis of this magnetic coupling.

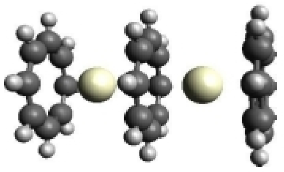

Figure 1: [Ce$_2$ COT$_3$]$^{2-}$

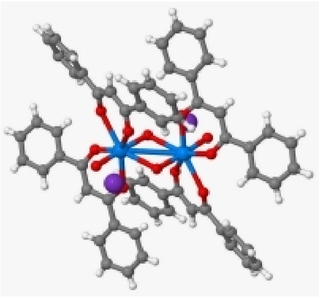

Figure 2: [(UO$_2$)dbm$_2$ ·K]$_2$

I will present our results on a 4f-4f dimer of Cerium(III) (Fig. 1), and a 5f-5f dimer of Uranium(V) (Fig. 2). These molecules are described using correlated wave functions based theory. The analysis of these calculations permits to determine i) the nature and magnetic properties of the local magnetic centers ii) the coupling between these centers which in each case is strongly anisotropic iii) the pathway of the magnetic coupling. In order to recover the experimental coupling, highly correlated CI methods have to be used. All calculations are simulated using Spin Hamiltonians.

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Simulating Electron Transfer in Biomolecules: the Role of Polarization and Long-range Electrostatic Interactions

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Photo-induced electron transfer is ubiquitous in biological processes, including photosynthesis and respiration. Interestingly, it has been recently shown that magnetosensing by Drosophila flies and possibly by other animals is mediated by flavoproteins cryptochromes, undergoing photoactivation via a series of photo-induced electron transfer events. In this talk, the challenges theoretical chemistry faces when one wants to describe energetics and dynamics of electron transfer in complex heterogeneous media, as proteins, will be discussed. Specifically, the role of environment polarization and long-range electrostatic interactions in accurate evaluation of such quantities as redox potentials, charge-transfer states excitation energies, and electronic couplings, using a cryptochrome protein as a model system, will be addressed. A new software for identifying electron transfer pathways in proteins, eMap, will be introduced.

Lecture: Lec-17

Calculation of X-Ray Absorption and Photoemission Spectra of Molecules in Complex Environment

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I will present recent results of the calculation of N K-edge absorption spectra and N1s Photoemission spectra of triazine molecules in gas phase and adsorbed on a gold surface.[1] The calculations were performed with the Vasp[2] code and the projector augmented wave approach (PAW)[3]. The main advantage of the periodic scheme in the present context is that the metal surface or the triazine monolayer can easily be included in the calculations. With the same method, we have performed C1s and Ru3d photoemission spectra calculations for Ru complexes in aqueous solution. This work is part of a theory-experiment collaboration to probe the the electrochemical properties of molecular electrocatalysts in aqueous environment by means of in operando spectroscopy employing synchrotron-based X-ray photoelectron spectroscopy (XPS). The photoelectron spectra were measured by means of a liquid jet. We have focused our study on the model system $[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ showing a unique fingerprint of the higher valence *ruthenium oxo* species in the XPS spectra, in relation to the oxidative reaction pathway. In addition to the transition potential approach[5], we have also used *ad hoc* cut water clusters, computed by Monte Carlo simulations to account for the aqueous environment surrounding the complexes.

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The linearized *GW* density matrix

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The electronic Green's function contains much information, much more than the mere quasiparticle energies. For instance, by contracting the time variables, one obtains the density matrix. Further contracting the space variables, one gets the electronic density. The density matrix gives a direct access to many physical observables: the kinetic energy, the exchange energy, the Hartree energy, the electric field, etc.

Using the *GW* approximation to the self-energy [1], we have obtained a compact expression for the density matrix that we have named linearized *GW* density matrix [2]. It allows one to obtain an improved density matrix (and density) directly from "one-shot" calculations. In other words, it is meant as a cheap approximation to the self-consistent *GW* without actually performing the self-consistency.

The approximation has been implemented in MOLGW [3], a Gaussian basis *GW* code. The performance of this approximation has been tested on a benchmark of 34 molecules. It gives excellent densities, Hartree, and exchange energies [4], better than quasiparticle self-consistent *GW* (QS*GW*) [5]. When used to evaluate the Fock operator, the linearized *GW* density matrix improves the ionization potential for some simple molecules, such as N_2, by as much as 0.5 eV!

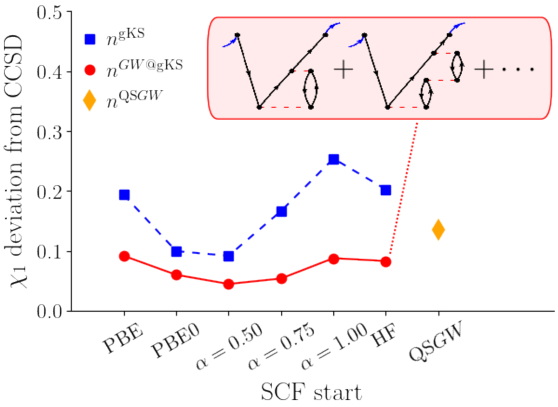

Figure 1: Error in the electronic density averaged over 34 small molecules for different density matrices as a function of the starting mean-field approximation.

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Multi-scale Modeling of Chemistry in Water

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Molecular dynamics simulations of chemical reactions in water can be significantly accelerated by exploiting the local nature of chemical reactivity, and describing a reactive region at the quantum mechanical (QM) level, while the environment is described at the more approximate molecular mechanical (MM) level. The challenging aspect of such simulations is the diffusive nature of the solution, with water molecules that flow in and out of the reactive region. Over the past decade several QM/MM models have appeared; Constrained QM/MM models in which the QM water molecules are constrained within a reactive region, and adaptive QM/MM models in which the water molecules change description as they flow across the QM/MM boundary. These approaches have the potential to extend the impact of QM/MM far beyond the rigid (bio) systems for which it is now predominantly used. The different models have varying degrees of complexity and (inversely related) accuracy, but there is currently no one model that has been adopted as a widespread molecular modeling tool. I will discuss some of the main bottlenecks to widespread application, present our new developments on both adaptive and constrained models, and compare performances of the different approaches in describing nucleophilic addition reactions in water.

High-Dimensional Quantum Dynamics of Functional Organic Polymer Materials: Coherence, Confinement, and Disorder

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This talk addresses quantum dynamical studies of ultrafast photo-induced energy and charge transfer in functional organic materials, complementing time-resolved spectroscopic observations [1] which underscore that the elementary transfer events in these molecular aggregate systems can be guided by quantum coherence, despite the presence of static and dynamic disorder. The intricate interplay of electronic delocalization, coherent vibronic dynamics, and trapping phenomena requires a quantum dynamical treatment that goes beyond conventional mixed quantum-classical simulations. Our approach combines first-principles parametrized lattice Hamiltonians [2], based on TDDFT and/or high-level electronic structure calculations, with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [3] and its multi-layer (ML-MCTDH) variant [4], along with semiclassical methods [5]. The talk will specifically focus on (i) the elementary mechanism of exciton migration in oligothiophene (OT) model systems representative of the poly(3-hexyl thiophene) donor material [5-7], (ii) the creation of charge transfer excitons in stacked, regioregular $(\mathrm{OT})_n$ assemblies [8-9], and (iii) exciton dissociation and free carrier generation in regioregular donor-acceptor assemblies [2,9]. Special emphasis is placed on the influence of structural (dis)order and molecular packing, which can act as a determining factor in transfer efficiencies. Against this background, we will comment on the role of temporal and spatial coherence along with a consistent description of the transition to a classical-statistical regime [7].

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Environment Contribution to Molecular Spectroscopy, Reactivity and Photochemistry.

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The combination of quantum mechanics (QM) with molecular modeling (MM) is a powerful tool for studies of simple and complex liquids. In addition, it may also be used to study the spectroscopic and reactivity of molecules in solution, a situation that is germane in chemical laboratories. The understanding of the solvent effects is thus a major concern in the rationalization of experimental results. In the last two decades theoretical treatments have been developed to incorporate solvent effects. An important direction of research uses some sort of computer simulation to perform hybrid calculations. This is generally called QM/MM method, because both classical and quantum methodologies are employed. In fact the simulations can be performed both at the classical (e.g. Monte Carlo or Molecular Dynamics) or quantum levels (e.g. Born-Oppenheimer Molecular Dynamics). As long as the thermodynamic condition can be imposed this opens a large avenue for applications in other parts of the phase diagram. Hence, it is also possible to address the technologically and environmental friendly condition of supercritical fluids. A simple protocol where the quantum mechanics calculations are performed subsequent on structures generated by the liquid simulations has been developed along the past years and guarantees efficiency and statistical convergence of the results [1]. Different applications have been made in spectroscopy and reactivity both in regular liquid environment as well as in supercritical condition. A critical review of this sequential QM/MM using either Monte Carlo or Born-Oppenheimer Molecular Dynamics will be presented based on a large variety of applications [2-10] on absorption and emission spectroscopy, magnetic shielding related to NMR experiments, excited state dynamics of simple organic molecules, simple chemical reactions as well as some photophysical processes. Some perspectives will also be presented.

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Aqueous solutions: a look at the surface

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In aqueous solutions the acid-base chemistry at the surface can be quite different from that in the bulk; this aspect is of great importance for several processes. For instance, the presence of surfactant molecules in the atmosphere is known to influence the nucleation process and hence the creation of droplets that ultimately form clouds. Amino acids are water-soluble organic compounds that can play such a role. Originating from phytoplankton and bacteria, they are injected into atmospheric droplets over oceans by bubble bursting.

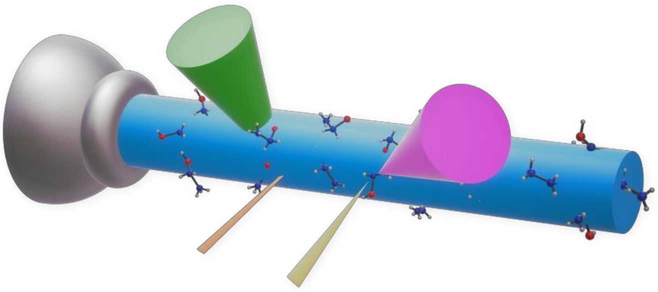

Figure 1: X ray photoemission from a micro-jet of an aqueous solution of cysteine.

By a joint experimental and theoretical study, an aqueous solution of cysteine is here taken as a prototype system to explore distribution and protonation states of such amino acid. It is shown how both properties, which are, of course, strongly affected by the average acidity of the environment, also exhibit large differences between surface and bulk. X-ray photoelectron measurements at N1s and S2p edges are interpreted by means of reactive molecular dynamics simulations for predicting the composition of the aqueous solution at different pH and by quantum calculations for predicting the binding energies and the chemical shifts. At specific pH values, we find that the distribution of the cysteine species at the surface is quite different from that of the bulk, for the appearance in the surface region of species, containing the COOH group, which do not exist in the bulk. Likewise, we predict the occurrence at the surface of “low pH species”, containing NH_3^+ and SH groups, which do not exist in the bulk of medium/high pH solutions This finding, however, cannot be used to infer straightforwardly that the surface propensity of H+ is different from that of the bulk of the aqueous solution.

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COLLOCATION METHODS FOR COMPUTING VIBRATIONAL SPECTRA

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When the potential energy surface (PES) does not have a special form (e.g. a sum of products), it is common to use quadrature to compute a vibrational spectrum. Direct-product quadrature grids are most popular. The size of a direct-product grid scales exponentially with the number of atoms and it is not not possible to store values of the PES for molecules with more than 5 atoms. One option is to use a Smolyak quadrature grid. In this talk, I shall present collocation methods with Smolyak-type grids. Collocation has advantages: 1) point selection is less important; 2) no integrals, no quadratures, no weights; 3) easy to use with complicated kinetic energy operators; 4) it can be used with any (the best possible) coordinates and basis functions; 5) in many cases fewer collocation than quadrature points are required; 6) the length of the vectors one must store is reduced. Collocation can be used with the Multiconfiguration Time-Dependent Hartree (MCTDH) approach. The collocation-based MCTDH method I shall present can be used with general potential energy surfaces. This is imperative if one wishes to compute very accurate spectra. When the basis is good, the accuracy of collocation solutions to the Schroedinger equation is not sensitive to the choice of the collocation points. The original collocation-MCTDH (C-MCTDH) method [J. Chem. Phys. 148, 044115 (2018)] uses, as is also true in standard MCTDH, a direct product basis. Because we do not rely on having a sum-of-products potential energy surface, we also have a direct product grid. By using generalized hierarchical basis functions, that span the same space as the single particle functions we introduced in the first C-MCTDH paper, and a Smolyak grid, we have developed C-MCTDH approach that makes it possible to prune both the basis and the grid.

Lecture: Lec-24

Simulating Biological Systems Coupling Particles and Fields with Molecular Dynamics

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The hybrid particle-field with molecular dynamics (hPF-MD) is a newly-established methodology based on density-functional potentials for the simulations of molecular systems [1]. Thanks to its low computational costs, hPF-MD is capable of treating large-scale soft matter systems using relatively small high-performance architectures [2]. As case examples, I will present the first hPF-MD model for peptides, showing how it is able to sculpt the main features of the folding diagram for model hydrophobic-polar sequences [3]. Then, I will introduce advances in the fundamental electrostatic theory for density-field in both homogeneous and non-homogeneous dielectrics [4]. This is a crucial ingredient to expand the application range of hPF-MD to a large variety of biological systems, which are characterized by a strong polar/ionic character.

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Melting of the 2D Wigner Crystal

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Wigner crystals (i.e. a solid composed of only electrons) have been suggested to be stable in semiconductor interfaces, on the surface of liquid helium, and in graphene bilayers but there have been no direct studies of its stability taking Fermi statistics into account. We have performed restricted path integral Monte Carlo (PIMC) simulations [1] for the spin-polarized and unpolarized homogeneous electron gas in two dimension at low densities and low temperatures. We obtain the conditions for stability of the Wigner crystal by directly observing freezing and melting. The phase diagrams show both thermal and quantum melting. The thermal melting is mediated by a hexatic phase. A Pomeranchuk effect is found for unpolarized case. This complements the previous study of the melting of the Boltzmannon Coulomb crystal [2]. We will discuss the method to perform these Path Integral simulations and compare with previous estimates for the 2D Wigner crystal stability.

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Efficient Modeling of Thermal and Quantum Fluctuations in Materials and Molecules

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Both electrons and nuclei follow the laws of quantum mechanics, and even though classical approximations and/or empirical models can be quite successful in many cases, a full quantum description is needed to achieve predictive simulations of matter.
Traditionally, simulations that treat both electrons and nuclei as quantum particles have been prohibitively demanding. I will present several recent algorithmic advances that have increased dramatically the range of systems that are amenable to quantum modeling: on one hand, by using accelerated path integral schemes to treat the nuclear degrees of freedom [1], and on the other by using machine-learning potentials to reproduce inexpensively high-end electronic-structure calculations. I will give examples of both approaches, and discuss how the two can be used in synergy to make fully quantum modeling affordable [2].

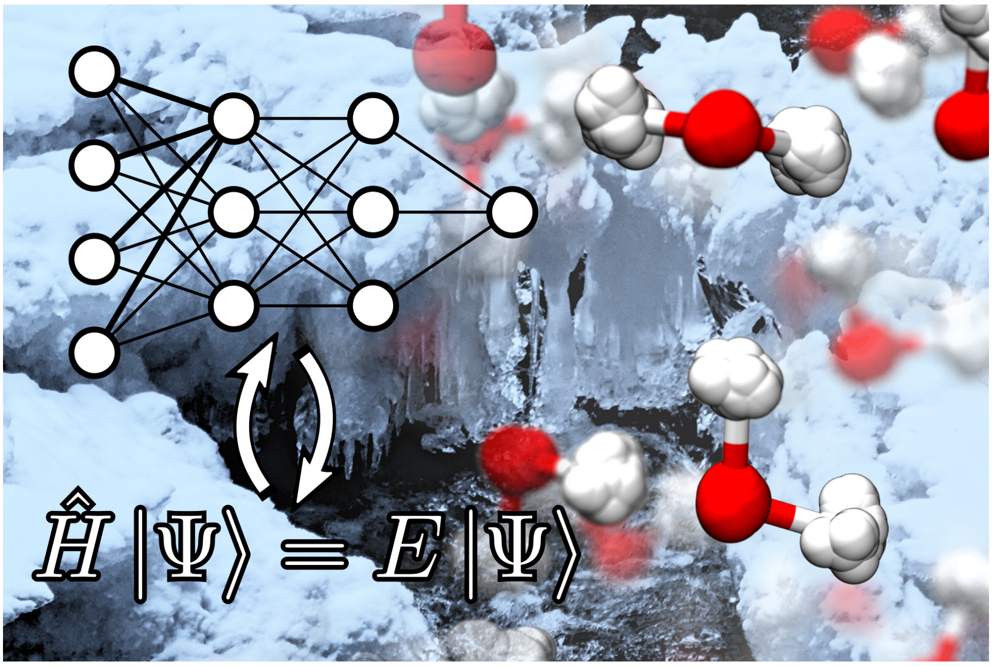

Figure 1: A combination of machine-learning potentials and accelerated simulations of quantum nuclei enable a first-principles description of the thermodynamics of solid and liquid water.

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Progress in quantum embedding in the condensed phase

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I will discuss recent progress in quantum embedding approaches based on density matrix embedding and dynamical mean-field theory in ab initio descriptions of condensed phase systems.

Modeling Photo-Responsive systems using combined classical and DFT approaches

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Photo-responsive materials are gaining ever-increasing attention thanks to their fast -- and often dramatic -- response and the relatively non-invasive nature of light as a stimulus [1].
Nonetheless, understanding the excited state mechanisms that are at the basis of these materials is very challenging both for theory and for experiments. If indeed ground state properties of condensed systems (ex. crystalline or amorphous phases) are currently feasible and even if excited states description has greatly advanced [2,3,4] this latter is often associated with nontrivial computational expense so that the study of excited state reactivity, mechanochromism, piezochromism, heterogeneous photocatalysis, and photoemission, remains a significant challenge for theoretical approaches.
In this talk, we present the contribution of our group to the modeling of some of these phenomena, combining different theoretical tools ranging from classical to quantum approaches in either molecular or periodic formalisms [5-7]. We demonstrate that by choosing, developing and combining suitable theoretical tools, such phenomena can be qualitatively (or even quantitatively) described.

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Heavy Element Solution Chemistry – A Sojourn Through Ideal and Non-Ideal Solutions and Their Interfaces

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Heavy elements, including those actinides and lanthanides, often exist as highly charged ions that induce extended polarization across multiple solvation shells and organizational structure in solution.[1,2] Their metal-ligand complexes are also prone to supramolecular self-assembly facilitated by long-range electrostatic interactions with solvent or background electrolyte participation.[3] Tackling the solution chemistry of *f*-elements requires an in-depth understanding of electronic structure and hierarchical interactions they impose upon their surroundings. This work will discuss different strategies for performing condensed phase simulations of actinides and lanthanides in solution environments that systematically approach realistic conditions associated with purification and synthesis. Such work spans both *ab-initio* and classical molecular dynamics simulations and underpinning methods (e.g. the development of new polarizable potentials for An(III)). Further, we discuss the practical impacts of hierarchical interactions associated with actinides in realistic solutions, and how this challenges traditional computations that rely on well-understood energy landscapes and narrow ensemble distributions of solution phase environments.

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Quantum Tunnelling in Chemical Reactions

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This talk will describe recent theoretical and computational work in our research group on quantum tunnelling in chemical reactions.

Quantum tunnelling can have a major effect on the rate constants for hydrogen atom transfer reactions. The accurate calculation of tunnelling effects and the computation of rate constants remains a major challenge. This talk will describe research from our own group on predicting tunnelling effects in bimolecular and unimolecular reactions.

A method for predicting rate constants will be outlined which brings together quantum dynamical and quantum chemistry techniques in an efficient reduced dimensionality approach. Applications to the hydrogen atom transfer and exchange reactions of hydrocarbons will be described.

Secondly, recent developments in Semiclassical Transition State Theory (SCTST) [1] will be discussed. This will include the development and testing of a SCTST reduced dimensionality procedure with our benchmark quantum dynamical results. Application of SCTST to the unimolecular decay of Criegee intermediates will be described. In addition, an application to the decomposition mechanism of the highly toxic nerve agents sarin and VX will be presented.

The calculations described in the talk were performed by Xiao Shan, Sam Greene and Tim Burd from our research group.

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Machine Learning Models for Biomolecular Dynamics

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The last years have seen an immense increase in high-throughput and high-resolution technologies for experimental observation as well as high-performance techniques to simulate molecular systems at a microscopic level, resulting in vast and ever-increasing amounts of high-dimensional data. However, experiments provide only a partial view of macromolecular processes and are limited in their temporal and spatial resolution. On the other hand, atomistic simulations are still not able to sample the conformation space of large complexes, thus leaving significant gaps in our ability to study molecular processes at a biologically relevant scale. We present our efforts to bridge these gaps, by combining statistical physics with state-of-the-art machine learning methods to design optimal coarse models for complex macromolecular systems. We derive simplified molecular models to reproduce the essential information contained both in microscopic simulation and experimental measurements.

Lecture: Lec-32

Electrostatic Catalysis of Chemical Reactions

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Chemists appreciate that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, it was only recently that it was shown that an external electric field can also be used to catalyse non-redox reactions, thereby opening up a new dimension to chemical catalysis [1]. So-called electrostatic catalysis arises because most chemical species have some degree of polarity and so can be stabilized by an appropriately aligned electric field; when this occurs to a greater extent in transition states compared with reactants, reactions are catalysed [2]. However, by their nature such effects are highly directional and so implementing them in practical chemical systems is problematic. We have been using a combination of theory and experiment to explore various solutions to this problem. The first is using surface chemistry techniques, in conjunction with the break-junction technique in scanning tunnelling microscopy [1]. This allows us to detect chemical reaction events at the single molecule level, whilst delivering an oriented electrical field-stimulus across the approaching reactants. The second is making use of the electric fields within the double layers of electrochemical cells to manipulate both redox and non-redox unimolecular reactions. Here we find that molecules actually self-align and interact with electrolyte ions to facilitate catalysis [3]. Finally, in an approach that is truly scalable, we have instead addressed problem of orientation of the electric field by making use of appropriately placed charged functional groups to provide the electrostatic stabilization for solution-phase reactions [4]. In this way, the direction of the local field experienced by the reaction centre is fixed, and by associating the stabilization or destabilization with the protonation state of an acid or base group, it has the advantage of providing a convenient pH switch. In this talk our latest results will be presented and the prospects for electrostatic catalysis discussed.

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Simulation of strongly correlated systems with 2D tensor networks

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Tensor networks are a class of variational wave functions enabling an efficient representation of quantum many-body states, where the accuracy can be systematically controlled by the so-called bond dimension. A well-known example are matrix product states (MPS), the underlying tensor network of the density matrix renormalization group (DMRG) method, which has become the state-of-the-art tool to study (quasi-) one dimensional systems. Progress in quantum information theory, in particular a better understanding of entanglement in quantum many-body systems, has led to the development of tensor networks for 2D systems, including e.g. projected entangled-pair states (PEPS) or the 2D multi-scale entanglement renormalization ansatz (MERA). In recent years these methods have become very powerful tools for the study of 2D strongly correlated systems, in particular for models where quantum Monte Carlo fails due to the negative sign problem.

In this talk I report on recent progress with infinite projected-entangled pair states (iPEPS) - a two-dimensional tensor network ansatz for 2D ground states in the thermodynamic limit. I present simulation results for the 2D Hubbard model at 1/8 doping in the strongly correlated regime, where a close competition between a uniform d-wave superconducting state and different types of stripes states is found. From systematic extrapolations to the infinite bond dimension limit we conclude that a period 8 stripe state is the lowest energy state. Consistent results are also obtained by density matrix embedding theory, DMRG, and constrained-path auxiliary-field quantum Monte Carlo [1]. Furthermore I show that period 4 stripes - which are typically observed in experiments on the cuprates - become the ground state upon adding a realistic next-nearest neighbor hopping term to the Hubbard model [2]. Finally, I will briefly highlight other recent directions with 2D tensor networks, including an approach to study 2D quantum critical phenomena [3] and simulations at finite temperature [4].

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Molecular Properties and Interactions: A Wonderful Playground for a Theoretical Chemist

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Our understanding of the electronic structure of molecules often comes from spectroscopic investigations in which electromagnetic radiation is applied to a molecule and the scattering or absorption of the radiation is measured. These experimental techniques probe the structure and properties of molecules by observing their response to applied electromagnetic perturbations. Such measurements provide a detailed picture of molecular systems, often rich in detail and sometimes difficult to interpret.

Molecular electronic-structure theory has developed to a stage where it can be used to investigate a large number of molecular properties of increasing complexity, with control over the accuracy of the results, and provide invaluable help in the interpretation of experimental measurements of a broad range of molecular properties of importance in several scientific areas. Examples sampled from our recent and past efforts in this area will be presented.

Optical production of polyatomic complex in ultracold regime

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We explore the feasibility of using simple ultracold molecules as building block for larger polyatomic species. We focus on ultracold molecules that can be oriented in space by external fields (static electric or optical fields), and in particular those with small permanent electric dipoles and large quadrupole moments. We have shown in previous studies [1,2] that some heteronuclear bi-alkali diatomic molecules that have been cooled to ultracold temperatures have those properties. The interaction between such aligned molecules can be described by an anisotropic long-range expansion; the interplay between the different power-law contributions can lead to long-range wells that could sustain bound molecular complexes. De-excitation of approaching molecules could populate those complexes, allowing to study regimes often linked to roaming reactions.

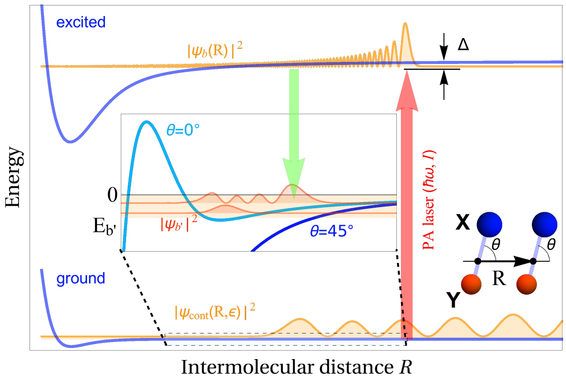

Figure 1: Scheme to produce tetramers; a pair of molecules excited by a laser may decay to form a bound molecular complex into a long-range well.

We present a detailed theoretical analysis for ultracold KRb and RbCs molecules, both of which were cooled and trapped successfully, resulting in production of $(\mathrm{KRb})_2$ and $(\mathrm{RbCs})_2$ complexes (see sktech in Fig. 1). We show that both systems can form rotational-vibrational loosely bound states near the molecular dissociation limit or in deeply bound long-range states, depending on the relative alignment of the interacting dimers. The proposed approach is based on universal properties of polar molecules and the conclusions can be generalized to the formation of polyatomic molecules starting from larger molecules with a favorable ratio of permanent dipole and quadrupole moments.

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Po-containing Molecules in Fusion and Fission Reactors

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Fission and fusion reactors can only play a role in the future energy landscape if they are inherently safe by design. For some reactor concepts, a major remaining issue is the undesired production of radiotoxic ^{210}Po. To filter out the volatile Po species, information on their molecular composition is needed. An experimental characterization is very challenging due to the large required amount of radioactive Po. An alternative quantum chemistry approach was taken to predict the temperature-dependent stability of relevant diatomic Po-containing molecules. Experimental data on lighter analogue molecules was used to establish a well-founded methodology. The relative occurrence of the Po species was estimated in the cover gas of (i) the leadbismuth eutectic coolant in the accelerator-driven MYRRHA fission reactor and (ii) the PbLi eutectic tritium breeder in the DEMO fusion reactor. In both systems, Po is found to occur mainly as PbPo molecules and atomic Po.

This work[1] illustrates how quantum chemistry for molecules can have impact on engineering decisions for large facilities.

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The Limits of Stability in Three-Body Coulomb Systems

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Negative atomic ions owe their existence to electron correlation. Exploring the correlated motion of electrons at low nuclear charge and capturing this behaviour in future theoretical method developments, such as correlation functionals, is an important step forward in ensuring new methods can address increasingly exotic and complex systems.

A number of proofs exist regarding the stability of a system with respect to the number of electrons, nuclei and charge [1]. In this talk, we explore the limits of stability for a three-body system interacting via Coulomb forces. Exploiting the series solution method with a Laguerre basis, we calculate high accuracy fully-correlated and Hartree-Fock energies and wavefunctions [2], before extending this fully-correlated ground state methodology to excited S states.

Additionally, we report a variational method for calculating the critical nuclear charge for binding two electrons in the ground state and excited S states of fully-correlated systems, explore the effects of nuclear motion, determine the critical nuclear charge for binding within the Hartree-Fock approximation, and calculate accurate electron correlation data at low nuclear charge Z (Figure 1) [3]; these data are available to download for benchmarking and new developments.

It will be shown that the nuclear charge required to prevent electron detachment increases as the nuclear mass decreases, that the outer electron remains localized at a finite distance from the nucleus as the binding energy of the outer electron approaches zero, the condition for the emergence of a secondary Coulomb hole, and that a minimum in the correlation energy occurs at $Z \approx Z_C^{HF}$.

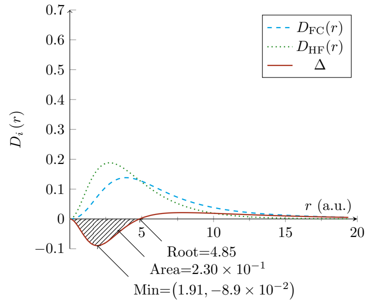

Figure 1: Coulomb Hole Δ *at* $Z = Z_C^{FC}$

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Stabilization of α-helices by side-chain to main hydrogen bonds. Can current force fields describe the hydrophobic shielding?

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Poly-glutamine (polyQ) rich tracts are common in transcription factors and their length determines several health disorders. The polyQ tract of the androgen receptor shows a surprisingly high helical content. We previously showed that this is caused by stabilizing side-chain to main-chain hydrogen bonds [1]. Here we use NMR and Molecular Dynamics to understand how the polyQ flanking residues affect these hydrogen bonds. We also explore to which extent current force fields can describe the hydrophobic shielding that is the source of the stabilization.

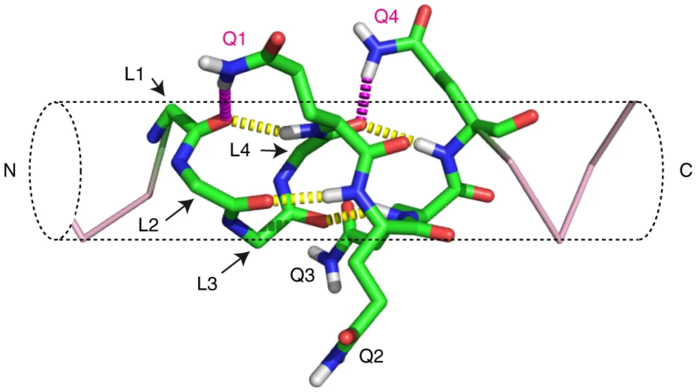

Figure 1: Conformation of a polyQ peptide showing some side-chain to main-chain hydrogen bonds stabilizing the α-helix.

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Quasistructural Molecules

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The notion of molecules and structures is central to our chemical understanding. One seemingly useful definition of molecules is that they correspond to minima on potential energy surfaces (PES) and the local PES must support at least one bound rovibrational state. The structure of a molecule is usually considered to be the geometry corresponding to the minimum. If a molecule exists and has a structure, it is also commonly accepted that its internal motions can be separated into vibrations and rotations, motions which usually have very different time and energy scales.

Nevertheless, there are chemical systems where both the notion of a molecule, that of a structure, as well as the separation of rotational and vibrational motion can be questioned. The lecture is centered around molecular ions and complexes[1-5] where the concept of a structure and the separation of vibrations and rotations seems to break down, yielding a quasistructural molecular with associated unusual nuclear dynamics. All of the following characteristics should hold, for a smaller or larger extent, for a molecular system to be considered quasistructural (from a high-resolution spectroscopic point of view): (a) the notion of a static equilibrium structure, corresponding to a minimum on the potential energy surface of the molecule, looses its strict meaning, (b) internal nuclear motions (rotations and vibrations) become dominant, resulting in an effective molecular structure often even qualitatively different from the equilibrium one, (c) separation of the internal nuclear motions breaks down, rotational and vibrational degrees of freedom cannot be separated from each other when interpreting even the lowest rovibrational states of the molecule, resulting in effective rotational constants drastically different from the equilibrium ones even for the ground vibrational state, (d) classification of the rovibrational states requires the use of permutation-inversion symmetry and molecular-symmetry groups, and (e) some of the rovibrational eigenenergies assigned to a vibrational parent state exhibit unconventional (in the most striking cases "negative") rotational contributions.

Sophisticated tools of the fourth age of quantum chemistry[6] are able to yield a quantitative understanding of the energy level structure and the high-resolution spectra of quasistructural molecules but it is certainly of interest to develop new models[7] to aid the qualitative understanding of nuclear motion dynamics of quasistructural molecules.

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QM/MM analysis of metalloenzymes: developments and applications

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(Dated: June 19, 2019)

Abstract

In this talk I'll discuss our studies of metalloenzymes using QM/MM simulations, including both DFTB3/MM free energy simulations and strategies to improve the results with higher level QM/MM energetics. I'll also touch upon several other technical issues such as the effect of QM region size and the degree of conformational sampling required for a meaningful mechanistic analysis; these will be illustrated with specific examples such as Catechol O-methyltransferase and Human U six biogenesis protein 1 (USB1). I'll then discuss our latest results regarding the mechanism of DNA polymerase and the potential role of the third Magnesium ion in catalysis.

Toward First Principles Simulations of Biological Matter under Ionizing Radiations

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The transient collision (10-17 s) of high-energy-transfer particles with biological matter results in ionization or excitation of its constituent molecules. Huge amounts of energy are deposited locally, typically several tens of eV. These early physical events produce a myriad of reactive radical species that are at the source of cascades of chemical processes spanning several spatial and temporal scales. The physical chemistry of these ultrafast processes are not well understood at the present time. During this seminar I will introduce an original set of methodologies that we have devised to investigate these phenomena from first principles [1,2]. These are based on Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) and Ehrenfest Molecular Dynamics (MD) simulations. A hybrid scheme coupling these approaches to polarizable force fields have been devised to simulate large biological systems. This implementation includes explicit time propagation of the electric fields mediating interaction between the quantum and classical parts of the system[3] Theses methodologies have been implemented in deMon2k. Our approach allows simulations of collisions of molecules with HET, and subsequent ionization, ultrafast charge migration, energy relaxation/dissipation on the attosecond time scale (cf. Figure). Ehrenfest MD further gives access to non-adiabatic chemical reactivity taking place in the first femtoseconds after irradiation. I will introduce the methodologies and applications to various questions of current high interest in radiation chemistry.

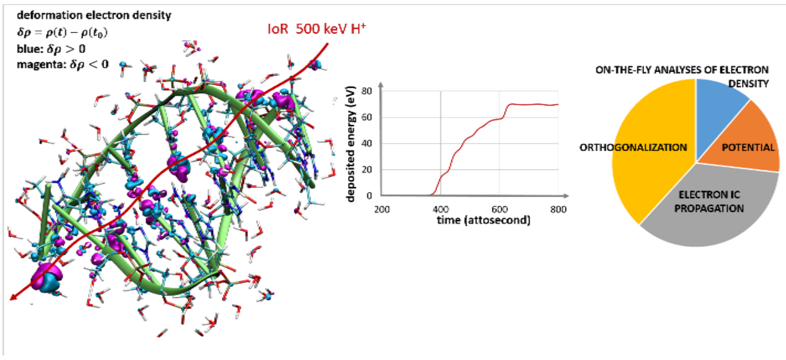

Figure : Irradiation of 10-base DNA double strand by a 500 keV proton particle The left panel depicts isosurfaces of the deformation density just after irradiation. On the right panel a graph shows the increase of deposited energy as a function time (middle) and the main computational tasks involved in the simulation (right)

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Photostability of Uracil affected by RNA environment or shaped light

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Uracil is a key unit of nucleotides in RNA, and thereby one of the crucial players in processing genetic information. As other genetic materials it is susceptible to light, which can lead to unwanted modifications within the chemical structure and finally to photodamage. In the present work, we will use light to investigate to which extend the inherent molecular properties of Uracil, like its photostability, can be influenced and whether it can be connected to the response of Uracil to fluctuation in its the natural environment.

Quantum optimal control theory is used to design laser pulses, either to accelerate or to delay the passage towards the conical intersection between S_2- and S_1-state from where the fast relaxation to the groundstate starts. Our results demonstrate how both can be achieved [1]. When Uracil is embedded in its natural RNA environment we observe similar features. For this purpose, we employ an approach that combines wavepacket dynamics with molecular dynamics [2,3]. The influence of different combinations of neighboring nucleobases on the photostability of Uracil is discussed. While mostly the relaxation time corresponds to the gasphase situation, sometimes significantly delayed lifetimes emerge, comparable to the previously light induced changes. To the further inspect the role of the correlated electron nuclear dynamics at the S_2/S_1 conical intersection, we further investigate its controllability via CEP control induced by a few cycle pulse.

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From Machine-Learning Interatomic Potentials to Atomic-Scale Materials Science

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Understanding the links between structure and properties in materials is one of the most central challenges for computational physics, chemistry, and materials science. Atomic-scale simulations based on density-functional theory (DFT) have played important roles in this – but they are computationally expensive and can describe structurally complex materials only in small model systems. Novel interatomic potentials based on machine learning (ML) have recently garnered a lot of attention in computational physics, chemistry, and materials science: these simulation tools achieve close-to DFT accuracy at only a fraction of the cost.

In the first part of this talk, I will argue that ML-based interatomic potentials are particularly useful for studying materials with complex structures, such as amorphous (non-crystalline) solids. I will describe an ML potential for amorphous carbon **[1]** that was built using the Gaussian Approximation Potential (GAP) framework **[2]**, with a special view on what is needed to create and validate ML potentials for the amorphous state. I will present recent applications of GAP-ML models to porous and partly "graphitised" carbons that are relevant for batteries and supercapacitors **[3]**, and to amorphous silicon, where ML-driven simulations allowed us to unlock long simulation times and accurate atomistic structures **[4]**.

In the second part, I will point out possible directions for the automated exploration and “learning” of condensed-phase potential-energy landscapes. We have recently introduced an ML-driven approach to inorganic crystal structure prediction, dubbed GAP-driven random structure searching (GAP-RSS) **[5]**. This technique, iteratively exploring and fitting structural space, allowed us to create to a flexible and accurate interatomic potential for elemental boron **[5]**, and more recently to develop a more general computational framework that can explore and fit potential-energy surfaces for different materials **[6]**. These early results are hoped to enable a more widespread use of ML-driven materials simulations in the years to come.

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Quantum Chemistry Assisted by Machine Learning

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In my talk I will show how machine learning (ML) assists quantum chemical research in a variety of ways. First, machine learning can be used to improve the accuracy of low-level quantum chemical (QC) method either by explicitly correcting their predictions as in Δ-learning approach[1] or by improving the semiempirical QC Hamiltonian as in parameter learning technique.[2] Second, ML can be used for very accurate representation of potential energy surfaces, *e.g.* to drastically cut the number of high-level QC calculations required for predicting rovibrational spectra with spectroscopic accuracy[3] or to perform excited-state nonadiabatic dynamics simulations at very low computational cost[4-5]. For carrying out this research I develop *MLatom*[6-7] program package optimized for efficient and user-friendly use of kernel ridge regression-based ML in atomistic simulations.

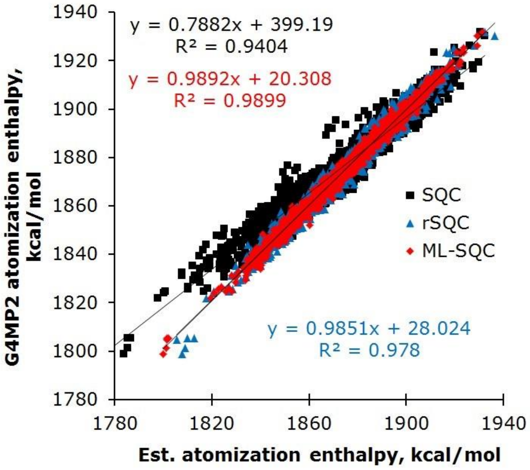

Figure 1: ML significantly improves semiempirical QC Hamiltonian.[2]

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Unraveling the Role of Non–Covalent Interactions in Recognition and Catalysis

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Intermolecular forces, including hydrogen bonding, ion-pairing and π-interactions, are being increasingly recognised as crucial factors determining selectivity in numerous recognition and catalytic processes. Excellent examples include protein-binding processes, asymmetric hydrogen-bonding and counteranion-directed catalysis. In parallel, new possibilities for biomimetic catalysis have also been demonstrated using multicomponent assemblies. Despite these promising results, a molecular understanding of these interactions in condensed-phase and their influence in the reaction outcome remains challenging.

In this talk, I discuss some of the inherent challenges involved in the quantitative characterization of these interactions in solution and our ongoing work to overcome them. I will present examples in the area of protein recognition and supramolecular chemistry, which have provided us with a deeper understanding of the critical influence of non-covalent interactions for reactivity and selectivity.

Unveiling the chemical reactivity of sulfide mineral surfaces in the presence of water and oxygen.

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Modeling chemical reactions that occur in the solid/water interfaces is challenging. A realistic model of the solid/water interface must include aspects such as surface reconstruction, defects in the solid, water dissociation, pH and ionic strength.

We have successfully modelled the oxidation mechanism of pyrite, FeS_2, (Fig 1a) in the presence of water and oxygen using Density Functional/Plane Waves calculations[1]. Pyrite oxidation is an important environmental issue related to the mining of noble metals such as gold, copper and uranium. The oxidation of sulfide minerals leads to the formation of sulfuric acid contributing to the acidification of aquifers and, hence, the remobilization of heavy metals to the environment. We have shown that the adsorbed water on the surface has an important role participating in the oxidation process through an intricate sequence of reactions that can be summarized as shown in the Fig. 2. The experimental results are now adequately understood in terms of our proposed oxidation mechanism.

The arsenopyrite, FeAsS (Fig. 1b) is normally found associated to pyrite. The presence of the arsenic replacing one of the sulfur atoms have been subject of debate. It is shown that the presence of the As in the pyrite structure, will avoid some of the necessary steps to oxidize the arsenopyrite favoring its oxidation[2]. Furthermore, the pyrite/arsenopyrite interface form a galvanic pair that promotes the oxidation of the arsenopyrite with respect to the pyrite[3]. The stability and the band offset of the pyrite/arsenopyrite interface explains why the pyrite favors the oxidation of the arsenopyrite.

The sulfur oxidation due to the reconstruction of the chalcopyrite ($CuFeS_2$) surface[4] with the formation of sulfide dimer and the formation of two dimensional crystal covellite (CuS) will be also discussed[5].

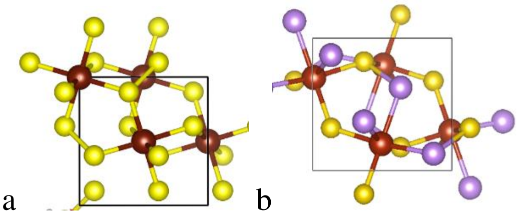

Figure 1. Structure of a) pyrite and b) arsenopyrite. Sulfur in yellow, arsenic in blue and iron in red.

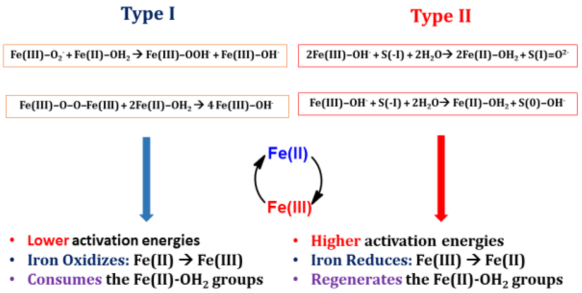

Figure 2. The types of reactions that occur on the pyrite surface in the presence of water.

Acknowledgments: CNPq, CAPES, FAPEMIG, RENOVAMin, INCT-ACQUA.

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Ultracold doubly-polar molecules: on the way to create them via a Laser-Assisted Self-Induced Feshbach Resonance

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Controlling the scattering properties between ultracold alkali-metal atoms and alkaline-earth or ytterbium atoms (with a closed-shell (^{1}S) ground state) offers fascinating perspectives like the realization of topological phases of matter [1], novel Efimov states with systems of large mass imbalance, or the formation of ultracold polar paramagnetic molecules which are promising for instance for quantum simulation of lattice-spin systems [2]. It has long been thought that if one of the atoms has no magnetic moment, magnetic Feshbach resonances (MFR) could not be observed. A subtle coupling mechanism has been recently invoked to predict MFRs between paramagnetic Rb(^{2}S) and non-magnetic Sr(^{1}S) atoms [3, 4]. The observation of the resulting very narrow MFR remains however challenging [4].

We propose a new type of Feshbach resonance (FR): the Light-Assisted Self-Induced Feshbach Resonance (LASIFR), where the closed and open coupled channels characterizing the FR are both associated with the electronic ground state of a heteronuclear diatomic molecule, which possesses an intrinsic permanent electric dipole moment (PEDM) varying with the internuclear distance. A sub-THz photon couples the pair of ultracold atoms, occupying for instance the lowest motional state of an optical lattice site, to a bound rovibrational state close to the dissociation limit. The resonant pattern becomes obvious in the field-dressed-state picture, which formally maps the scheme of a MFR.

The interspecies scattering length can then be controlled by both the intensity and the detuning of the photon frequency with respect to the transition one. A frequency chirp across the resonance can be engineered to fulfill the adiabaticity criterion for the complete population transfer toward the molecular bound level. Like with a "regular" MFR, a STIRAP can be followed for transferring the population to the absolute ground state. We exemplify this proposal with the case of RbSr, based on our investigations on the structure of this molecule [5, 6].

The similarities of the proposed approach with previous works (see for instance [7, 8]) will also be discussed.

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In the last years, we have developed a computational methodology to simulate charge transfer processes in complex systems. Due to the large system size, which has to be treated quantum mechanically, we have developed a coarse-grained quantum/classical methodology, which allows to describe the dynamics of the electronic system coupled to the dynamics of environment, e.g. the protein in water solvent. Charge-transfer (CT) parameters are computed using a fragment orbital approach applying the approximate Density Functional method SCC-DFTB. Environmental effects are captured using a combined quantum mechanics/molecular mechanics (QM/MM) coupling scheme and dynamical effects are included by evaluating these CT parameters along extensive classical molecular dynamics (MD) simulations. Using this methodology, the time course of the charge can be followed by propagating the hole wave function using the time dependent Schrödinger equation for the Tight Binding Hamiltonian, which can also be used to compute the transmission and current through e.g. DNA nano-wires. The photo-activation of E. coli Photolyase involves, after photoexcitation of the chromophore and energy transfer to FAD, a long range hole transfer along a chain of Trp residues. Since this process could not be modelled using Marcus theory with parameters computed with classical equilibrium MD simulations, we used fully coupled non-adiabatic (Ehrenfest/surface hopping) quantum mechanics/molecular mechanics (QM/MM) simulations. The most recent extension concerns applications to charge and exciton dynamics in organic materials,

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From High-Resolution Spectroscopy to Light-Dressed Molecules

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We report new developments in the general quantum-dynamical code GENIUSH [1,2], originally invented to variationally solve the time-independent rovibrational Schrödinger equation for N-atomic molecules using a general and exact kinetic energy operator, arbitrarily-chosen vibrational coordinates and body-fixed frame embeddings. The up-to-date version of GENIUSH includes time-dependent quantum-dynamical features and is able to solve the time-dependent Schrödinger equation for molecules coupled to time-dependent external electric fields. The power of the theoretical framework developed is demonstrated by new time-dependent rovibrational results for the coherent inhibition and enhancement of tunneling in ammonia isotopomers, both achieved by nonresonant laser fields [3]. These time-dependent quantum-dynamical computations rely on the concept of light-dressed states, treat all rotational and vibrational degrees of freedom in a numerically exact way and assume neither the alignment nor the orientation of the molecule under investigation. If time permits, we will also present novel results for the spectroscopy of light-dressed polyatomic molecules with an emphasis on the signature of light-induced conical intersections [4] on light-dressed spectra [5].

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Time-Resolved Measurement of Interparticle Coulombic Decay Processes

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Interparticle Coulombic Decay (ICD) processes are electronic decay processes of weakly interacting systems, which are initiated by inner-valence excitation ionized ionization. These weakly interacting systems include solvents, biomolecules and quantum dots in semiconductors, that interact via electron correlation. We report about a new theory for the time-resolved description of the spectator resonant ICD processes initiated by and measured with short laser pulses. We propose to excite the system with an XUV laser pulse, measure the absorption spectrum of the system and to quench the decay process with a strong IR laser pulse at different time delays. The quenching results in the initiation of an ICD process, whose ICD electron signal can then be measured without interference effects. Additionally, the lifetime regime of the ICD processes allow for the observation of oscillations of the time- and energy-differential ionization probability close to the peak energy of the RICD electron signal. We propose to utilize this oscillation for the measurement of lifetimes of electronic decay processes.

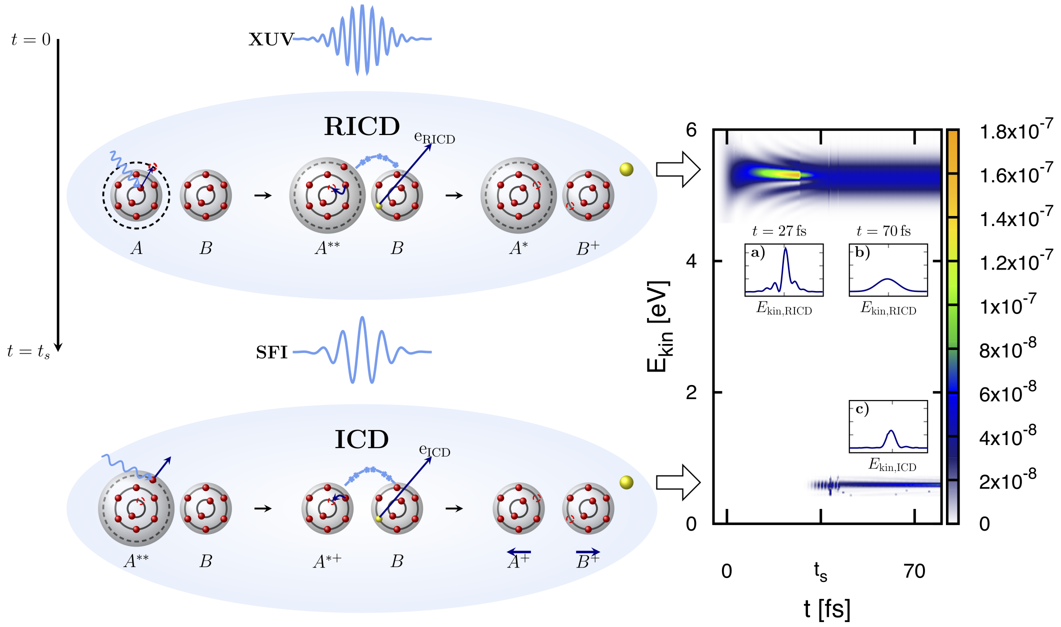

Figure 1: Illustration of the proposed measurement and the underlying processes.

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Pursuing accuracy in intermolecular potentials and spectra

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We obtained a new, highly accurate ab initio ground-state intermolecular potential-energy surface (IPES) for the CO-N_2 complex [1]. Thousands of intermolecular geometries were selected using a Gaussian-quadrature approach. The corresponding interaction energies were calculated with the CCSD(T) method and Dunning's aug-cc-pVQZ basis set extended with a set of 3s3p2d1f1g midbond functions and were fitted to an analytical function.

The symmetry-adapted Lanczos algorithm was used to compute rovibrational energies (up to $J = 20$) for the new IPES. The RMSE with respect to experiment was found to be on the order of 0.038 cm^{-1} which confirms the high accuracy of the potential. This level of agreement is among the best reported in the literature for weakly bound systems and considerably improves on those of previously published potentials.

In the second part of the talk, I will show results on the reparametrization of semiempirical potentials to improve the description of non-covalent interactions within the MOPAC program. For this, we use as benchmark ab initio CCSD(T) interaction energies.

To end, I will present preliminary results on vibrational circular dichroism spectra of phenylacetylenes.

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Machine learning a highly accurate exchange and correlation functional of the electronic density

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In recent years a lot of progress has been made in the study of water and its different phases. Empirical methods are progressing to the point of being better than first principle methods, thanks to the unlimited degrees of freedom allowed in more and more complex force fields and the availability of better accurate data. These methods are however limited in their scope, and completely incapable of being generalized or of treating reactive environments. At the ab-initio level, to reach chemical accuracy, one often has to rely on hybrid functionals, thereby limiting the size of systems for which simulations are feasible. Several attempts have been made in the past to solve this problem. Most approaches try to re-parametrize the exchange part of the generalized gradient approximation (GGA) functional. However, it turns out that one of the main deficiencies of GGA, namely its self-interaction error, places an upper bound on the accuracy of these techniques. Here, we propose a new framework to create density functionals for electronic structure calculations by using supervised machine learning. These machine learned functionals are built on top of well-established and physically motivated density functionals and are designed to correct their shortcomings. We show that our functional can lift generalized gradient methods to the accuracy of coupled cluster calculations for small organic molecules, all while being highly data-efficient and somewhat transferable across chemical systems. We further test our method on water, where it accurately reproduces results for both gaseous and condensed systems.

CatLab – Putting calculation before experiment in organometallic catalysis

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Computational studies of homogeneous catalysis play an increasingly important role in furthering (and changing) our understanding of catalytic cycles and can help to guide the discovery and evaluation of new catalysts [1,2]. While a truly "rational design" process remains out of reach, detailed mechanistic information from both experiment and computation can be combined successfully with suitable parameters characterising catalysts [3] and substrates to predict outcomes and guide screening [4].

The computational inputs to this process rely on large databases of parameters characterising ligand and complex properties in a range of different environments [5-8]. Such maps of catalyst space can be combined with experimental or calculated response data [7], as well as large-scale data analysis. Rather than pursuing a purely computational solution of *in silico* catalyst design and evaluation, an iterative process of mechanistic study, data analysis, prediction and experimentation can accommodate complicated mechanistic manifolds and lead to useful predictions for the discovery and design of suitable catalysts. In this presentation, I will use examples drawn from our recent work, including the early stages of our development of a reactivity database, to illustrate this approach.

Website: https://feygroupchem.wordpress.com/

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The force awakens in quantum Monte Carlo

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While quantum Monte Carlo methods are routinely employed to predict accurate total energies of relatively large systems, a major limitation has been the lack of efficient schemes to obtain energy derivatives. Here, we capitalize on a simple and general formalism we have recently developed to overcome this limitation and compute interatomic forces and other derivatives in quantum Monte Carlo with the same numerical scaling as computing the energy alone in the sampling process. These developments allow us to consistently optimize the wave function and the structural parameters in quantum Monte Carlo, and explore the performance of the method in combination with different choices of Jastrow-Slater wave functions. In particular, we show that the use of a selected-configuration-interaction scheme to generate compact and balanced determinantal components for multiple states leads to the fast and accurate computation of ground- and excited-states structures as well as vertical and adiabatic excitation energies in quantum Monte Carlo.

MRChem: Quantum Chemistry at the basis set limit with Multiwavelets

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The accuracy of Density Functional Theory calculations is governed by two factors: the **functional** employed and the **basis set**.

Despite the great popularity and success of some very well known functionals, the universal functional remains elusive. A vast number of functionals is currently available, sometimes tailor-made to target specific systems or properties. Assessing the accuracy of a modern functional, requires also a basis set which is capable of achieving an even greater precision – ideally approaching a complete basis – efficiently and systematically.

The two main families of basis sets (plane waves and Gaussian-type orbitals) have drawbacks which limit them, especially when high precision is required. A very attractive alternative is constituted by by grid-base methods[1] such as Multiwavelets[2, 3]. They combine conceptual simplicity (basis functions are standard polynomials) with the ability to reach complete basis set results within any given, predefined precision. Multiwavelets are fully orthonormal (like plane waves) and localized (like Gaussian-type orbitals).

With the development of MRChem,[4] – a multiwavelet code – we have been able to carry out extensive benchmarks of energy and properties, consistently achieving the basis set limit[5, 6].

In this presentation, we will summarize the theoretical multiwavelet framework, with emphasis on our implementation of the SCF optimizer and linear response solver, we will give an overview of some recent applications, and we will discuss the hurdles which shall be overcome to extend the Multiwavelet framework to large systems (thousands of electrons or more).

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Conformational heterogeneity in enzymatic catalysis and evolution

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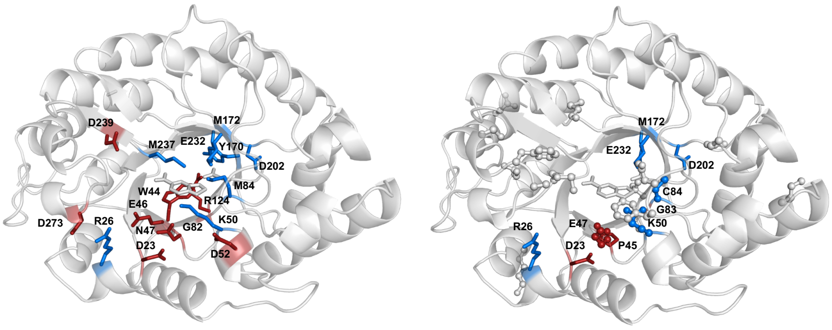
De novo enzyme design has been a long-term dream for industrial applications, while still presents a challenge for computational methods. It requires a fundamental understanding of enzymatic catalysis and those evolutionary forces, which optimize catalytic rates [1]. We explored the links between conformational plasticity and enzyme evolvability using multiscale and coarse-grained approaches [2]. We simulated the laboratory evolution of two Kemp eliminase designs (KE07 and HG3.17) and have demonstrated that optimization of reorganization energy is a major driving force of catalytic improvements [1-3]. At the same time, we identified multiple catalytically relevant configurations, and showed that conformational heterogeneity persists throughout the evolutionary trajectories. In particular, we demonstrated that simultaneous presence of alternative rotamers in HG3.17 are required to reproduce the experimentally observed barriers. We further showed that catalytic rates are robust to significant changes in the conformational ensemble; which promotes reducing promiscuous activities. We relate conformational diversity to co-evolving dynamical couplings [4], and propose that these two phenomena jointly shape the functional repertoire of enzymes in the cellular environment [5].



HG.3

HG.3.17

Figure 1: Residues with significant contributions to reorganization energy in the designed (HG.3) and evolved (HG.3.17) Kemp eliminase. Unfavorable contributions ($\lambda \geq 0.5$ kcal/mol) are displayed in red, favorable contributions ($\lambda < -0.5$ kcal/mol) are in blue.

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Multireference Methods for Extended Systems

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I will describe our latest progress in combining density matrix renormalization group (DMRG) with pair-density functional theory (PDFT) as a new way to calculate correlation energy. Calculations that require active spaces larger than the feasibility limit of the conventional complete active-space self-consistent field (CASSCF) method will be presented. I will also report our advancements in using density matrix embedding theory (DMET) in combination with localized active space self-consistent field (LASSCF) [1] as a solver and its application to realistic models of strongly-correlated systems.

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Simulating energy conversion processes from first principles

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We describe recent progress in describing heterogeneous, defective materials with complicated morphologies using first principles methods, including electronic structure calculations and ab initio molecular dynamics. We focus on two examples: interfaces for solar energy conversion processes, and materials composed of complex building blocks, e.g. assemblies of nanoparticles used in colloidal solar cells. We aim at showing the importance of unraveling mechanisms and providing fundamental, physical insights, in order to pave the way to material design strategies.

The polyspherical approach: applications to spectroscopy

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The polyspherical coordinates allow one to describe motions of large amplitude In a flexible and systematic way. We will present applications to penta-atomic systems and to the Eigen cation in full dimensionality (33D).

X-ray Raman scattering of liquids

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Local probes of the electronic ground and valence excited states are essential for understanding hydrogen bonding in aqueous environments. Vibrational infra-red (IR) spectroscopy is an established technique for investigations of hydrogen bonding. High-resolution X-ray absorption spectroscopy [1] and resonant inelastic X-ray scattering (RIXS) [2] offers a complement to IR vibrational spectroscopy. The propagation of the nuclear wave packet in dissociative core-excited state results in the long vibrational progression seen in both theory and experiment. This gives great advantage of RIXS in comparison with IR spectroscopy which probes mainly the first OH excitation. We show how different resonant inelastic X-ray scattering (RIXS) channels deliver separate information; about the local structure via long-range dynamics in quasi-elastic RIXS and about short-range dynamics, which is much less sensitive to the structure, in the electronically inelastic 1b1 and 4a'' channel in water and methanol, respectively. Our theoretical framework is composed of classical ab initio molecular dynamics (MD) simulations, calculation of local potential energy surfaces from the sampled configurations, and quantum wave packet modeling of the nuclear motion in relevant degrees of freedom. Thereby, we reach insights into the variations in the local HB environment, which strongly affects the long-range part of the OH potential energy curves (PEC). For enhanced insight, we derive the distribution of PECs of OH bonds with intact and broken HBs as reconstructed from experimental RIXS data of liquid water. In contrast by analysis of the dynamic mechanisms, we show that the splitting, emerging for pre-edge core-excitation, has a purely dynamical origin and is primarily sensitive to the short-range part of the PEC since the splitting of the 1b1 and 4a'' peaks is formed at short time-scales before fragmentation.

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Potentialities of Wavelet formalisms for large-scale DFT calculations and beyond

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The BigDFT software package implements since few years a linear scaling Kohn- Sham density functional theory (LS-DFT) optimization algorithm based on Daubechies wavelets, where a minimal set of localized support functions are optimized in situ and therefore adapted to the physico-chemical properties of the system under investigation.

One key factor influencing the accuracy and cost of DFT is the choice of basis set, where minimal, localized basis sets compete with extended, systematic basis sets. Wavelets offer both locality and systematicity and are thus ideal for representing an adaptive local orbital basis which may be exploited for LS-DFT [1]. One may also make further approximations, e.g. dividing a system into fragments [2] or exploiting underlying repetition of local chemical environments [3], where each approximation may be controlled and quantified. This ability to treat large systems with controlled precision offers the possibility of new types of materials simulations [4].

We will demonstrate the advantages of wavelets as a basis for large scale DFT calculations, as implemented in BigDFT code. We illustrate, from a general perspective, a quantitative method to identify and assess the partitioning of a large quantum-mechanical system into fragments. We will then conclude our discussion by presenting some case-studies among which the example of materials for organic LEDs, showing how our approach may be used to account for environmental and statistical effects on excited state calculations of disordered supramolecular materials [5].

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Photo-processes in biological systems – Need for hybrid QM/MM with polarization

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Photo-processes in biology are fundamental to life itself, e.g., photosynthesis and light harvesting. However, accurate description of such processes is challenging, especially considering the need to depict the complex environment with sufficient accuracy. It requires a large number of degrees of freedom to be described and therefore, become impossible for any ab initio or purely quantum mechanical method. Hybrid quantum mechanical molecular mechanical (QM/MM) methods, that combine the accuracy of quantum mechanical methods and the speed and versatility of molecular mechanical methods, are used for these systems. Effective fragment potential (EFP) is a sophisticated, polarizable and non-empirical molecular mechanical method that is capable of treating the long range electrostatics and short range non-covalent interactions with sufficient accuracy. On the other hand, these systems are multi-reference in nature, and therefore, multireference electronic structure methods, such as spin flip MP2 and equation-of-motion coupled cluster or MP2 (EOM-CC or EOM-MP2) need to be used. We have developed hybrid methods based on EFP and EOM-MP2. In this talk, I will present some applications of the hybrid techniques to understand the excited state processes, especially in biological systems. I will also discuss our work on developing polarizable force fields based on machine learning techniques that can be applied to biological systems.

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Q-MP2-OS: A new approach to correlation using quadrature

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As computational hardware becomes ever more massively parallel, quantum chemical methods and their underpinning implementations must evolve. In this lecture, I will present a novel algorithm [1] for the computation of the opposite-spin (OS) MP2 correlation energy, which is well suited to large-scale parallelization.

The method combines deterministic numerical quadratures and screening techniques, and entirely avoids the computation of any two-electron integrals. Speedup, scaling and accuracy results for a variety of molecules and reactions reveal that the new algorithm achieves 1 kcal/mol accuracy with almost perfect parallelizability (Fig. 1) and a computational cost which grows only quadratically with system size.

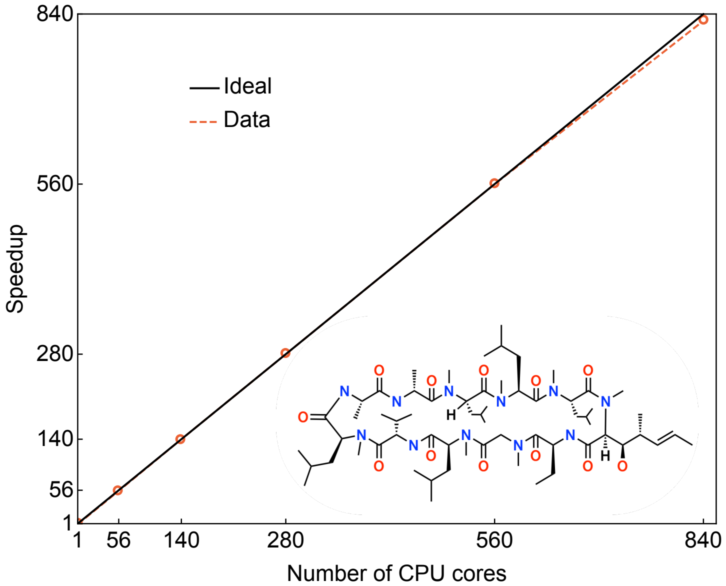

Figure 1: Speedup curve for Q-MP2-OS/6-31G on cyclosporine.*

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Wavelets for electronic structure calculations, an introduction and overview

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Haar wavelets will first be presented to illustrate the basic principles of multiresolution analysis. Then I will introduce three families of wavelets that are useful in the context of electronic structure calculations. Daubechies wavelets have unique properties as a basis set for representing wavefunctions. Interpolating wavelets are very well suited for the solution of partial differential equations, such as Poissons equation. Multiwavelets allow for an easy grid refinement and are therefore well suited to perform all-electron calculations. In addition I will give an overview over several wavelet based libraries of the BigDFT package and some non-standard functionalities of the BigDFt code for exploring potential energy surfaces.

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Large-scale Ab Initio Simulations with Orbital-free Density Functional Theory

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Orbital-free (OF) density functional theory (DFT), rooted in quantum mechanics but involving only the non-interacting electron density, is an especially promising tool for large-scale electronic structure calculations. Achieved by circumventing the wavefunction operations required for conventional Kohn-Sham (KS) DFT, the two main advantages of OFDFT are speed and (quasi-)linear computational scaling with increasing system size. However, these advantages come at a cost in accuracy in the calculation of: i) the non-interacting electron kinetic energy, $T_{s;}$ and ii) the electron-ion (screened nucleus) interaction term, E_{ext}, in the form of local pseudopotentials (LPSs). Significant efforts have been made over the years to overcome both obstacles with meaningful success.

We discuss various approaches for improving approximations to T_s, which include recent work on the local, gradient-based kinetic energy density of nearly free electrons by the derivation of new response functions, as well as the use of hybrid techniques that include localized atom-centered density matrices within the usual OF formalism. We also report advances in constructing accurate LPSs employed in E_{ext} using global optimization techniques based on genetic algorithms.

We conclude by presenting a recent application of our OFDFT-code, PROFESS, in a molecular dynamics study of liquid Sn that confirms the existence of a second excitation mode in the collective dynamics, as well as its theoretical explanation through mode coupling.

Excited state dynamics of transition metal complexes using efficient trajectory surface hopping methods.

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Modelling excited state dynamics of transition metal complexes is challenging for different reasons: the many degrees of freedom, the large number of near degenerate electronic excited states, and last but not least, the difficulties of electronic structure methods to describe accurately the energy and character of different electronic excited states. In this lecture I will describe our most recent efforts to use trajectory surface hopping (SH) methods [1] to model the photophysical dynamics of several transition metal complexes. To alleviate the huge costs of such calculations, we have recently coupled SH to linear vibronic coupling (LVC) models [2]. The combination of LVC within SH offers extreme computational efficiency [2], allowing even to run SH for these large systems with different setups. Besides time-resolved chemical insight, this marriage offer opportunities for methodological benchmarks. On the one hand, SH can be used to identify essential degrees of freedom and electronic states that could be employed in a quantum MCTDH wavepacket propagation in reduced dimensionality. On the other, a comparison of SH with MCTDH dynamics with the same LVC model allows to question the validity of several assumptions of SH.

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Rydberg polyatomic molecules: Electronic structure and experimental proposal for their creation

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The traditional Rydberg molecules are formed by a tightly bound positively charged core and an excited electron circulating around it. A more exotic type of Rydberg molecules were theoretically predicted to exist when a ground-state atom locally probes the Rydberg electronic wavefunction [1]. These ultralong-range exotic species were experimentally observed in 2010 [2], showing that, analogously to Rydberg atoms, they have a large sensitivity to external field, which allows their control. Another type of ultralong-range Rydberg molecules are theoretically predicted to exist if a heteronuclear diatomic molecule, a Λ-doublet or a rotating polar molecule, is immersed into the wave function of a Rydberg atom [3, 4, 5, 6]. The anisotropic scattering of the Rydberg electron from the permanent electric dipole moment of the polar molecule is responsible for the binding mechanism in these Rydberg molecules. In this talk, we describe the main properties of these exotic ultralong range Rydberg molecules formed by a Rydberg atom and a heteronuclear diatomic molecule. We explore the electronic structure of triatomic Rydberg molecules formed from a potassium or rubidium Rydberg atom and the KRb molecule. These Rydberg molecules could be created by exciting Rydberg atoms in a mixture of ultracold atoms and ultracold molecules, i.e., molecules such as K-KRb or Rb-KRb would be created experimentally. We have found adiabatic few-GHz-deep electronic states evolving from the Rydberg degenerate manifold with a significant contribution from a low angular momentum Rydberg state, and having several vibrational bound states [7]. We propose a protocol to create these molecules experimentally in these electronic states from a mixture of ultracold atoms and ultracold molecules [7].

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Strong-coupling limit in DFT and Hartree-Fock: kinetic correlation energy and dispersion

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The strong-coupling expansion of DFT provides mathematical insights on how to build approximations that can describe strong correlation. In this talk I will discuss some recent developments, particularly the extension of this limit to the case of Hartree-Fock theory and the inclusion of dispersion.

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New Tight-Binding Quantum Chemistry Methods for the Exploration of Chemical Space

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The GFN-xTB family of semi-empirical tight-binding methods, which are variants of the well-known DFTB approaches, is introduced. The methods follow a global and element-specific parameters only strategy and are consistently parameterized for all elements through radon. Their original purpose and main target for the parameter optimization has been the computation of molecular geometries, vibrational frequencies, and non-covalent interactions. Very recently, the original GFN-xTB has been extended by including multipole electrostatic as well as one-center exchange-correlation terms leading to higher accuracy (at lower empiricism) specifically for non-covalent interactions and conformational energies[1]. A new, much faster (speedup of 3-5) first-order form employing classical electrostatics is briefly described (GFN0-xTB) The most sophisticated GFN2-xTB approach which furthermore employs density dependent D4 dispersion, is effectively used in the framework of meta-dynamics (MTD) to globally explore chemical compound, conformer, and reaction space[2]. The biasing potential given as a sum of Gaussian functions is expressed with the RMSD in Cartesian space as a metric for the collective variables. For typical conformational search problems of organic drug molecules, the new MTD(RMSD) algorithm yields lower energy structures and more complete conformer ensembles at reduced computational effort. Because TB methods (when combined with the Fermi-smearing technique) can also describe difficult electronic situations at least qualitatively correct, chemical reaction space exploration in a virtual nanoreactor also for transition metal containing systems is routinely possible.

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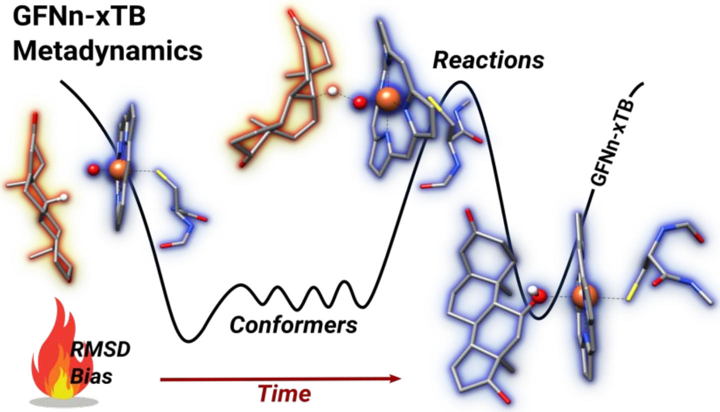

Potential energy surfaces and Berry phases from the exact factorization: A rigorous approach to non-adiabatic dynamics

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The starting point of essentially all modern electronic-structure techniques is the Born-Oppenheimer (BO) approximation. It not only makes calculations feasible, the motion of nuclear wave packets on the lowest BO potential energy surface often provides us with an intuitive picture of chemical reactions and, for small-amplitude motion, yields an excellent way to determine vibrational spectra. To go beyond the adiabatic limit is notoriously difficult. Here we present a novel approach to non-adiabatic effects that is based on the exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these wavefunctions lead to a unique definition of *exact* potential energy surfaces as well as *exact* geometric phases, both in the time-dependent and in the static case. We discuss a case where the exact Berry phase vanishes although there is a non-trivial Berry phase for the same system in Born-Oppenheimer approximation [2], implying that in this particular case the Born-Oppenheimer Berry phase is an artifact. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3]. This makes the classical force on the nuclei jump from one to another adiabatic surface, reminiscent of Tully surface hopping algorithms. Based on this observation, we propose novel mixed-quantum-classical algorithms whose unique feature is that the trajectories are coupled. Without recourse to Tully surface hopping and without any added decoherence correction, the new algorithm provides a rather accurate, (much improved over surface hopping) description of decoherence [4]. This is demonstrated for the photo-induced ring opening of oxirane [5]. We present a multi-component density functional theory [6,7] that provides an avenue to make the fully coupled electron-nuclear system tractable for very large systems. Finally, we use the approach to deduce an ab-initio electron-phonon interaction, and we explore the possibility of describing non-adiabatic effects in, e.g., proton transfer by R-dependent nuclear masses [8].

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Atomistic Simulation of Biomolecular Function: Ribosomal Translation, Ligand Binding Heterogeneity, and a Dynasome Perspective

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Ribosomes are highly complex biological nanomachines which operate at many length and time scales. We combined single molecule, x-ray crystallographic, and cryo-EM data with atomistic simulations to elucidate how tRNA translocation and the action of antibiotics work at the molecular level. We describe a new combined allosteric mechanism for erythromycin-induced translational stalling of the antibiotics sensor peptide ErmB.

Using streptavidin/biotin as a model system with super-strong affinity, we show that the underlying free energy landscape which governs ligand binding and unbinding can be extracted from combined atomic force microscopy (AFM) and force probe simulation data, which covers loading rates of 11 orders of magnitude. We will, finally, take a more global view on the 'universe' of protein dynamics motion patterns and demonstrate that a systematic coverage of this 'Dynasome' allows one to predict protein function.

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Recent progress in applying periodic coupled cluster theory to solids and surfaces

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This presentation will review recent progress in applying periodic coupled cluster theory to *ab initio* studies of solids and surfaces. We will discuss techniques that reduce the computational cost by accelerating the convergence of calculated properties towards the complete basis set as well as the thermodynamic limit using a plane wave basis [1-3]. We will present a diagrammatic decomposition of the coupled cluster correlation energy that makes it possible to correct for the basis set incompleteness error in a computationally efficient manner [1]. These developments have enabled an increasing number of *ab initio* studies and allowed for assessing the accuracy of coupled cluster theories by comparing to experimental findings as well as quantum Monte Carlo results. The presented applications will include phase transitions of solids [4] and molecular adsorption energies [5-7].

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A Machine Learning Shortcut to Physics-Based Modeling and Simulations

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The process of creating new chemistry and materials is increasingly driven by computational modeling and simulation, which allow us to characterize compounds of interest before pursuing them in the laboratory. However, traditional physics-based approaches (such as first-principles quantum chemistry) tend to be computationally demanding, in which case they may not be a practically viable option for large-scale screening studies that could efficiently explore the vastness of chemical space.

In this presentation, we will show how we employ machine learning to develop data-derived prediction models that are alternatives to physics-based models, and how we utilize them in massive-scale hyperscreening studies at a fraction of the cost. Aside from conducting such data-driven discovery, we also employ data mining techniques to develop an understanding of the hidden structure-property relationships that define the behavior of molecules, materials, and reactions. These insights form our foundation for the rational design and inverse engineering of novel compounds with tailored properties.

We will highlight our work on physics-infused machine learning models that seek to improve the robustness and range of applicability of purely data-derived models; on adapting cutting-edge data science techniques for chemical applications (e.g., transfer learning, active learning, and advanced network architectures for deep learning); and on meta-machine learning, i.e., to (machine) learn how to apply machine learning in the chemical domain. We will also show how we use data science techniques to advance, augment, and correct traditional molecular modeling and simulation methods.

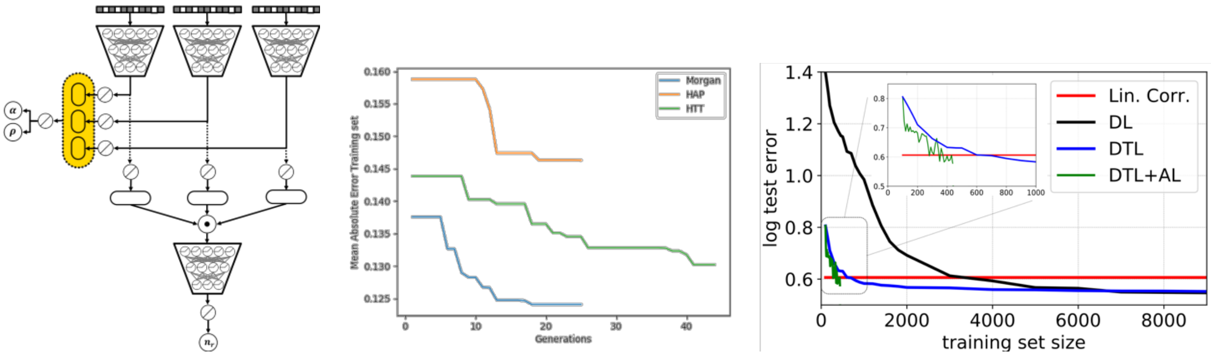

Figure. 2. (a) Network architecture that incorporates the non-linearity of the Lorentz-Lorenz equation; (b) ML model optimization within fixed features spaces for RI predictions via evolutionary learning; (c) Learning curves of traditional deep learning (DL) of static DFT polarizabilities vs DL plus transfer learning (DTL) vs DTL plus active learning (DTL+AL). The results demonstrate a dramatic reduction in the size of the required training set size.

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Multicomponent Quantum Chemistry: Integrating Electronic and Nuclear Quantum Effects

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Nuclear quantum effects such as zero point energy, nuclear delocalization, and tunneling play an important role in a wide range of chemical processes. Typically quantum chemistry calculations invoke the Born-Oppenheimer approximation and include nuclear quantum effects as corrections following geometry optimizations. The nuclear-electronic orbital (NEO) approach treats select nuclei, typically protons, quantum mechanically on the same level as the electrons with multicomponent density functional theory (DFT) or wavefunction methods [1]. Recently electron-proton correlation functionals have been developed to address the significant challenge within NEO-DFT of producing accurate proton densities and energies [2]. Moreover, time-dependent DFT and related methods within the NEO framework have been developed for the calculation of electronic, proton vibrational, and electron-proton vibronic excitations [3]. An effective strategy for calculating the vibrational frequencies of the entire molecule within the NEO framework has also been devised and has been shown to incorporate the most significant anharmonic effects [4]. Furthermore, multicomponent wavefunction methods based on coupled cluster and configuration interaction approaches, as well as multicomponent equation-of-motion coupled cluster methods for computing excited electronic and proton vibrational states, have been developed within the NEO framework [5]. These combined NEO methods enable the inclusion of nuclear quantum effects and non-Born-Oppenheimer effects in calculations of proton affinities, pK_a's, optimized geometries, vibrational frequencies, isotope effects, minimum energy paths, reaction dynamics, excitation energies, tunneling splittings, and vibronic couplings for a wide range of chemical applications.

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How to Make an Enzyme: Computational Optimization of Electric Fields for Better Catalysis Design

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We consider natural and de novo enzyme design and factors such as active site energetics, entropy of individual residues, dynamical correlations of enzyme motions, and electric fields as a way to exploit the entire protein scaffold to improve upon the catalytic rate. Using these principles, we show how other biomimetic catalytic constructs can be formulated, illustrated by a supramolecular capsule gold catalyst for carbon-carbon reductive elimination.

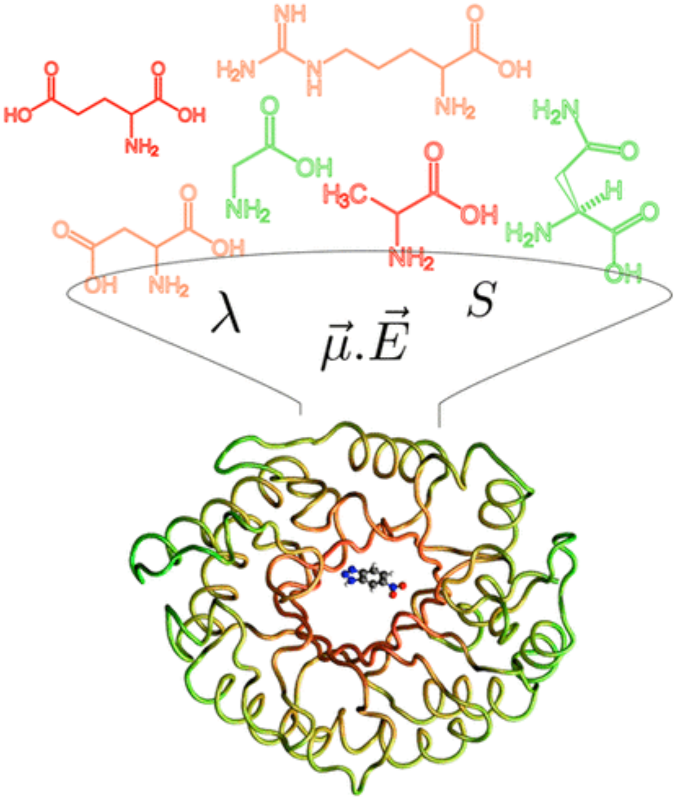

Figure 1: The origin of enzymes' remarkable performance has been the subject of extensive theoretical and computational research over the past several decades to design synthetic biocatalysts. This paves the way for building a unifying picture of the molecular interactions responsible for enzymes' incredible performance, hence managing efficient design and enabling further methods development for the accurate simulation of biomimetic catalysts.

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Explicitly correlated wave function approaches based on the random phase approximation

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Explicitly correlated wave function approaches have emerged as standard remedy for the slow basis-set convergence inherent to all orbital-based correlation methods. Especially in connection with coupled cluster theory, the F12 ansatz using Slater type geminals has proven as powerful approach, reducing computational timings due to drastically decreased basis-set sizes and thus enabling quantitative accuracy at feasible computational cost [1]. Complementing the line of already established F12 variants, we present explicitly correlated wave function approaches based on the random phase approximation (RPA). Even though RPA was originally developed to treat excited states in the context of density functional theory, it was later on found to be a promising orbital-dependent correlation method for ground-state energies, both capturing long-range dispersion and being, in contrast to perturbative approaches, stable for small-gap systems [2]. We show that the presented explicitly correlated RPA variants can be derived based on the method's connection to coupled cluster theory and that the gained improvement regarding basis-set convergence is comparable to the performance of state-of-the-art explicitly correlated coupled cluster approaches [3,4,5].

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Challenges for automated materials discovery

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This talk focuses on bottlenecks that we have identified in data-driven materials prediction.

In the first part, we describe a data-driven exporation of 2D materials, which was launched 5 years before the first serious fully automated high-throughput efforts and came up with some remarkable new discoveries that have been realized in experiment shortly afterwards, most notably noble metal dichalcogenides. The data repositories are poorly digitized and the striking question is: how can we extract information of some 100 years of laborous experimental work to make it useful for materials discovery?

In the second part I will focus on metal-organic frameworks (MOFs), the most prominent class of molecular-based framework materials. Built out of well-defined building blocks, machine-assisted data discovery appears to be straight-forward. We will show the components of our machinery, that allow to design a virtually infinite number of MOFs and other framework materials using a library-based building block approach. For property prediction, we suggest an alternative for structure encoding and decoding. We test the approach for predicting properties such as geometrical features, gas uptake and band gaps.

Egil Hylleraas — A Pioneer of Computational Quantum Mechanics

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The Norwegian physicist Egil A. Hylleraas (1898–1965) helped usher in the era of scientific computing by carrying out accurate calculations on the helium atom, thereby confirming the validity of quantum mechanics for more than one particle [1], by predicting the stability of the hydrogen anion, later detected in the Sun's atmosphere [2], and by performing the first calculation of the cohesive energy of a molecular crystal, LiH [3]. Many of the methods and techniques introduced by Hylleraas in the 1920s and 1930s are still important today. In particular, his treatment of electron correlation forms the basis for modern explicitly-correlated electronic-structure methods and F12 techniques. Hylleraas also performed many quantum-mechanical studies of small molecules and presented, for example, the first calculations of nuclear magnetic shielding constants of a molecule in 1950 [4].

Egil Hylleraas was the founding father of quantum chemistry in Norway. Indeed, in a public lecture on the chemical bond given in 1933, he stated (translated from the Norwegian) [5]: 'In closing my presentation, I hope to have convinced the audience of the far-reaching opportunities that now exist for establishing a theoretical chemistry, a quantum chemistry, on the same footing as the physical quantum theory.'

In this talk, an overview is given of the life and career of Egil Hylleraas, with emphasis on his scientific contributions and their relevance for modern theoretical chemistry.

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OH, ceriously, ... Molecules + materials = difficult!

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Materials and their surfaces and interfaces play crucial roles in our society and in the development of new technologies. Modelling such complex systems is by no means easy, and the computational scientist needs to make shrewd decisions about both (i) how to build *a structural model* that captures the complexity and imperfections of the real system at hand, and (ii) how to find an interaction model (say a DFT functional or a force-field) that is good enough. In particular, in this talk I will elaborate on the following topics with examples from water/solid interfaces, molecular crystals and metal oxide nanoparticles.

1. *Can we capture the chemistry of redox-active systems without including the electrons?*
   In the quest to reach larger and more complex systems sacrifices have to be made. Redox-active materials (with d and f elements) constitute a challenge for DFT calculations and force-field simulations alike and combining them in a *multiscale modelling* protocols is no easier! Is it possible to achieve a seamless linkage? Is it even possible to capture some chemistry without the electrons? Combinations of DFT, tight-binding-DFT, and reactive force-field models will be presented (see e.g. [1]). **Ceria** (CeO_2) is an example.

2. *Computational spectroscopy – as good as experiment?*
   Modelling is now an indispensable tool to decipher and interpret spectra and images produced from experiments, and adequate models for *post-processing* is as important as the data generation itself. I will discuss vibrational spectra in the context of AIMD simulations neural-network generated potentials and force-fields. **OH** groups, i.e. water and hydroxides, at solid/liquid interfaces [2] will be one example.

3. *How accurate are DFT methods for complex materials*?
   For condensed-matter systems of some complexity, there exists no quantum-mechanical or other theoretical method accurate enough to serve as a golden standard, so access to good-quality experimental data is crucial. Complex crystals can be promising benchmark systems as there often exist experimental structural data, the atoms stay put, and a large range of structural motifs is represented. [3]

I will also inform about the European Materials Modelling Council (https://emmc.info/), and our efforts to promote the use of materials modelling in industry and increase the trust in modelling results, and our efforts to seek a balance between physics-based and data-driven approaches.

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Intermolecular interaction energies from fourth order many-body perturbation theory. Impact of individual electron correlation contributions.

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The performance of Møller-Plesset perturbation theory methods for describing intermolecular interaction energies is investigated with the focus on illuminating the impact of individual electron correlation energy contributions in fourth order. While it is observed that for reproducing high level fifth order or coupled cluster interaction energies the inclusion of fourth order triples is mandatory, the decomposition of the fourth order singles (S), doubles (D), triples (T) and quadruples (Q) terms into their corresponding subterms revealed that individual terms from each excitation class can have a huge impact on the energy that is much larger than the total fourth order correlation contribution. A partial summation of S, D and Q terms can be derived that can reproduce the full fourth order interaction energies with a good accuracy and which does not include the computationally expensive triples energy term.

Path Integral Molecular Dynamics for Bosons

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Cold trapped atoms are fascinating systems, exhibiting fundamental physical phenomena and also potentially useful in emerging quantum technologies. We present a new method for simulating such systems using path integral molecular dynamics. The main difficulty in performing these simulations is enumerating all ring-polymer configurations that arise due to permutations of identical particles. For Bosons, we show that the potential and forces at each time step can be evaluated using a recurrence relation that avoids enumerating all permutations, while providing the correct thermal expectation values. The resulting algorithm scales cubically with system size. The method is tested and applied to Bosons in a 2D trap and agrees with analytical results and numerical diagonalization of the many-body Hamiltonian. An analysis of the role of exchange effects at different temperatures, through the relative probability of different ring-polymer configurations, is also presented.

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Multireference Configuration Interaction Beyond Singles and Doubles

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While Multireference Configuration Interaction including single and double excitations (MRCISD) remains a method of choice, or in some cases the only option, for accurate descriptions of reactions on excited state surfaces, the slow convergence of electron correlation for variational calculations and the lack of rigorous size-extensivity are hindrances. Efforts to extend the approach to beyond the single- and double-electron replacement approximation have been challenged by the loss of powerful graphical implementations for greater replacements than two. Although first-order perturbative approximations to MRCISD (i.e., MRCISD(TQ)) can be accomplished relatively efficiently using nongraphical techniques to evaluate e.g. a Löwdin partitioning of the Hamiltonian [1,2]

$$\begin{pmatrix} \mathbf{H}_{MM} & \mathbf{H}_{MQ_1} \\ \mathbf{H}_{Q_1M} & \mathbf{H}_{Q_1Q_1} \end{pmatrix} \left| \begin{matrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{matrix} \right\rangle - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{V}_{Q_1Q_1}\left(E_p^{SDTQ}\right) \end{pmatrix} \left| \begin{matrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{matrix} \right\rangle = E_p^{SDTQ} \left| \begin{matrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{matrix} \right\rangle$$

efforts to go beyond first-order are less straightforward. Particularly problematic is the selection of determinants (or configuration state functions (CSF)), which hold the promise of a relatively straightforward way of approaching the fully variational solution (or full CI) [3,4]. Using extensions of concepts originally developed for representing macroconfigurations, and in particular short macroconfigurations, it will be shown that a connected graph (or tree) in which vertices are representations of electron distributions (or configurations) using a non-standard positional numeral system provides sufficient structure to make arbitrarily high accuracy calculations feasible. As an example, calculations within 1 μH of full CI for a system of 10 electrons distributed over 24 orbitals can be run on a PC using pilot code. Moreover, since the large scale structure is organized by electron configurations, spin algebra can be implemented efficiently using a unitary group theoretical treatment with the proviso that Yamanouchi-Kotani states are used in lieu of the more familiar Gelfand-Tsetlin basis.

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Is Your Mechanism Correct?
Insights into Hydrogenation and Carboxylation Reactions

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Computational methods are increasingly applied to investigate reaction pathways. However, the proposed mechanisms are not always sufficiently validated. I will discuss the state-of-the-art in DFT modelling of metal-catalyzed reactions and show approaches to validate computationally proposed pathways.[1,2] Examples from two areas of organometallic catalysis are included: 1) **Hydrogenation**. In particular, recent insights into Co-catalyzed hydrogenation are discussed, where a mechanism proposed by us explains the experimental substrate preferences,[2] and 2) **CO_2 incorporation**. C-CO_2 bond formations with late transition metal complexes (e.g. Rh, Ni, Pd, and Cu) are discussed,[3,5] alongside a novel base-mediated reaction developed in our laboratory.[4] Based on our computational work, we propose trends as to when metal-CO_2 interactions should be expected during C-CO_2 bond formation.

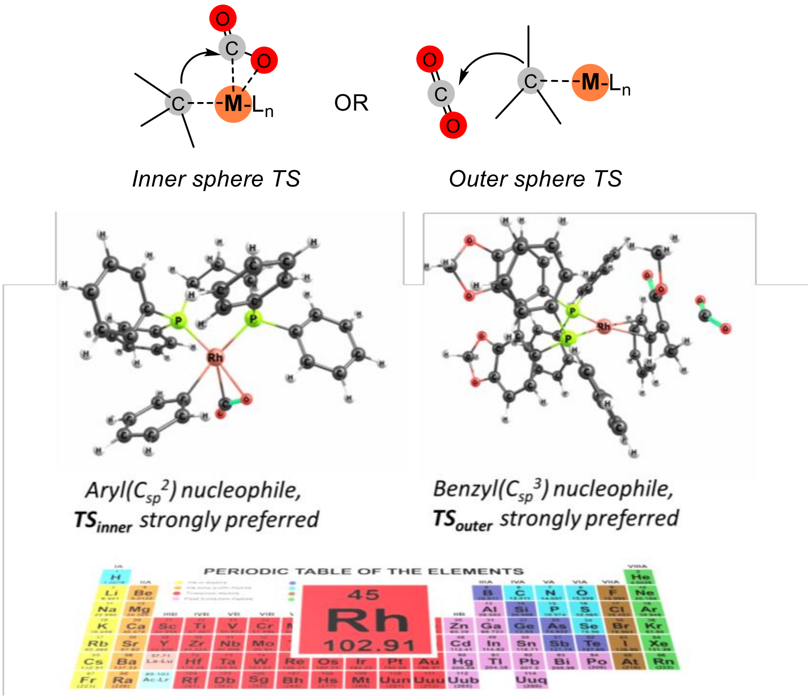

Figure 1. ***To bind or not to bind:*** *we present trends as to when metal-CO_2 interactions should be expected for C-CO_2 bond formation*[3-5]

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Machine learning for electron-transfer couplings

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For developing high-performance organic semiconductors, the understanding of their charge transport behavior is essential. Electronic coupling is a critical factor in determining the charge transfer rates. The values of electronic coupling could be varied by several orders of magnitude even with minor changes in intermolecular configurations. The sensitivity in molecular geometry makes it a critical test with machine learning (ML). In this work, we developed a ML-based approach to predict electronic couplings. We tested kernel ridge regression with the traditional and a simplified Coulomb matrix representation. The ML model trained can successfully reproduce the distance and orientation dependence with a mean absolute error of 3 meV for ethylene dimers. Most importantly, ML model saves 10–1000 times computational cost. With the help of ML, more reliable charge transport dynamics and prediction could be investigated in the future.

Bonding Pattern Change Induced by Relativistic Effects

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The periodic table provides a fundamental protocol for qualitatively classifying and predicting chemical properties based on periodicity. While the periodic law of chemical elements had already been rationalized within the framework of the nonrelativistic description of chemistry with quantum mechanics, this law was later known to be affected significantly by relativity. Here we report that relativistic effects change the bond multiplicity of the group 6 diatomic molecules M_2 (M = Cr, Mo, W, Sg) from hextuple bonds for Cr_2, Mo_2, W_2 to quadruple bond for Sg_2, thus breaking the periodicity in the nonrelativistic domain. Besides, we here also report a systematic theoretical study on the chemical bonding pattern change in the coinage metal dimers (Cu_2, Ag_2, Au_2, Rg_2) due to the relativistic effect on the superheavy elements. Unlike the lighter congeners basically demonstrating ns−ns bonding character ground state, Rg_2 shows unique 6d−6d bonding induced by strong relativity.

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Computational optical and X-ray spectroscopy studies for crystals & 2D materials

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I will present our recent computational spectroscopy studies for crystals and 2D materials. We simulated UV absorption, and vibrationally-resolved fluorescence and phosphorescence spectra for co-crystals of organic molecules[1] as well as metal-organic framework crystals to help elucidate the details of thermally-activated delayed fluorescence (TADF) photophysics. We simulated X-ray photoelectron (XPS) and absorption (XAS) spectra for crystals study the proton transfer reactions, and a series of carbon-based 2D materials, including graphene,[2] N-doped[3] and BN-codoped[4] graphene, graphdyine,[5] N-doped graphdyine,[6] and g-C_3N_4,[7] to understand effects of size, defect, doping, stacking. Calculations provide basic refence of representative local structures in such materials that can help clear assignments of experimental spectroscopies, and some general conclusions will be summarized.

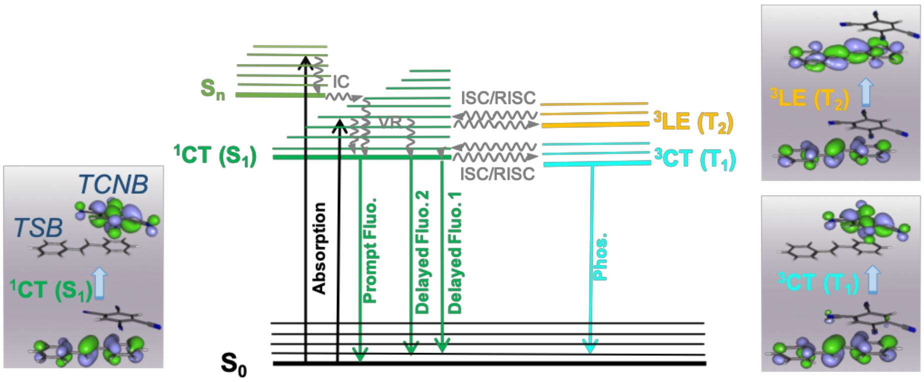

Figure 1: Jablonski diagram for the TSB-TCNB cocrystal. ISC/RISC via two channels S_1-T_1 and S_1-T_2 are responsible for the TADF. [1].

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New *ab initio* results for interaction-induced dipoles and susceptibilities and new analytical results for transition probabilities

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Absorption and emission of radiation occur during collisions of H_2 with H_2, H_2 with hydrogen atoms, and H_2 with helium atoms. Our *ab initio* results for the interaction-induced dipoles of these colliding species have astrophysical applications in analysing the radiative energy balances of star-forming regions of nebula; the outer stellar atmospheres of very old, very cool white dwarf stars; and the atmospheres of the outer planets and of exoplanets classified as "hot Jupiters" and "warm Neptunes." We have computed the interaction-induced dipoles of H_2-H [1] and H_2-H_2 by finite-field methods in UCCSD(T) and CCSD(T) calculations respectively, with aug-cc-pV5Z basis sets for production runs, and aug-cc-pV6Z and d-aug-cc-pV5Z basis sets for test calculations. For H_2-H, we have determined the interaction-induced dipoles for a total of nine H_2 bond lengths, 19 angles between the H_2 bond vector and the axis from the center of mass of H_2 to the H nucleus, and 16 separations between the centers of mass of H_2 and H, for a total of 2,736 geometrical configurations [1]. For H_2-H_2, we have determined the interaction-induced dipoles for 36 pairs of H_2 bond lengths, 17 geometrical configurations, and 15 separations between the centers of mass, for a total of 9,180 geometrical configurations. A subset of the H_2-H_2 dipole values have been tested by comparison with AUTOSURF results [2] obtained by Quintas-Sanchez and Dawes at CCSD(T)-F12b/VQZ-F12 level, with excellent agreement. We have expressed the results for the dipoles as series in the spherical harmonics of the orientation angles of the H_2 molecule(s) and the intermolecular vector, to separate contributions from different polarization mechanisms and to examine the convergence to the known long-range forms. In the collision-induced dipoles of both H_2-H and H_2-H_2, we have identified the effects of static charge moments beyond the quadrupole; and for H_2-H, we have determined the long-range van der Waals dispersion contribution to the dipole for the first time in an *ab initio* supermolecule calculation on this pair. We find excellent agreement between our long-range dispersion dipole and the $D_7 R^{-7}$ dipole computed by Bishop and Pipin using an explicitly correlated wave function for H_2 [3]. Additionally, in studies on H_2 in the ground singlet state [4] and the lowest triplet state, we have confirmed the convergence of the *ab initio* results to the known long-range analytical forms for the electrical moments and susceptibilities, through tensors of rank four. The corresponding moments and susceptibilities have also been obtained for O_2 in the ground triplet state, for use in analysing the collision-induced dipoles of O_2-O_2 in the singlet, triplet, and quintet states of the pair [5]. Recent analytical results for transition probabilities based on a separation of excited-state coefficients into their adiabatic and nonadiabatic components will also be presented [6].

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Neural networks learning quantum chemistry

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Historically, computational chemistry has been unable to overcome the orthogonal requirements of speed and accuracy. If you want an accurate calculation, be ready to pay the price in computer time. In the pursuit of a compromise between speed and accuracy many approximations were developed that expedite *ab-initio* methods with some loss of accuracy. Popular strategies include the partition of the system of interest into fragments, linear scaling, semi-empirical methods or the construction of empirical potentials that have been parametrized to reproduce experimental or accurate *ab-initio* data.

In this talk, we will present a fully transferable deep learning potential that is applicable to complex and diverse molecular systems well beyond the training dataset. Recently we introduced ANAKIN-ME (Accurate NeurAl networK engINe for Molecular Energies) or ANI in short. ANI is a new *method and sampling procedure* for training neural network potentials that utilizes a special kind of symmetry functions to build single-atom atomic environment vectors (AEV) as a molecular representation.

The AI methods that focuses on the use of large and diverse data sets in training new potentials, has consistently proven to be universally applicable to systems containing the atomic species in the training set. Focusing on parametrization for organic molecules (with CHNOSFCl atoms so far), we have developed a universal neural network potential which is *highly accurate compared to reference QM calculations at speeds* 10^7 *faster*. The potential is shown to accurately represent the underlying physical chemistry of molecules through various test cases including: *chemical reactions (both thermodynamics and kinetics), thermochemistry, structural optimization, and molecular dynamics simulations*. The results presented in this talk will provide evidence of the universal applicability of deep learning to various chemistry problems involving organic molecules.

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Searching for Super-Accuracy in Excited-State Calculations

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I will summarize recent efforts devoted to the definition of very accurate values for electronic excited states. For vertical transition energies, for which no comparisons with experimental data are available, I will show how high-level coupled cluster (CC) calculations (up to CCSDTQP) and selected configuration interaction (sCI) calculations (up to several millions of determinants) can provide very consistent estimates, of Full CI quality, for more than 100 states in compact compounds [1]. These reference data can be further used to benchmark several wave function methods in a very reliable way [1], including excited states presenting a strong double excitation character [2] Next, I will turn to comparisons with experimental data, and, more precisely 0-0 energies, for which I will show that chemical accuracy (errors smaller than 0.05 eV) can be reached almost systematically, even when geometries that are not extremely accurate are used [3,4]. Finally, I will discuss the quality of the excited state geometrical parameters that can be attained with various theoretical approaches [5,6], as well as their influence on the vertical fluorescence energies [7].

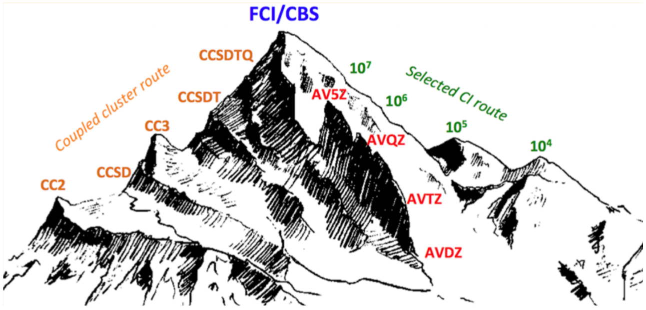

Figure 1: Illustration of the approach followed.

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Stability of Proteins in Solutions: A Microscopic Investigation on the Role of Surrounding Water/Cosolvent

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Preservation of protein's native folded form is important to conserve its biological activities. The folded native structure of a protein is highly sensitive towards the nature of solvent under specific environmental conditions. With the change of solvent's physicochemical properties protein's native structure can be disrupted.[1-2] Although water is a common solvent in biological systems that maintains the structure and function of proteins, the use of cosolvent in experiments has become popular due to their ability to solvate proteins quite efficiently. Further, in presence of cosolvent the stability of proteins can alter. Generally, cosolvents like some amino acids, polyhydric alcohols, sugars, trimethyl amine N-oxide etc., are used to conserve protein's native folded state and are known as osmolytes whereas urea, guanidinium hydrochloride, strong ionic detergents etc., are known as denaturant and are popularly used to denature protein's native folded state.

Studies have shown that the cosolvent effects on proteins are concentration dependent however there remains controversy. Moreover, despite significant efforts, the molecular mechanism of the action of cosolvents on proteins has been strongly debated in the literature. Therefore, the molecular-level understanding of the concentration dependent effects of cosolvent on proteins is of fundamental importance. In this presentation I shall discuss the behavior of a small protein in various monohydric alcohol-water binary mixtures at several alcohol concentrations under thermal stress.[3-6] This is essentially the study of cosolvent governed unfolding of a protein. Further, I shall discuss about the concentration dependent protein stabilizing efficiency of amino acids.[7] In all such work emphasis has been be given to identify the interaction that play major role to alter or preserve protein's structure. Our detailed discussion would shed light on competitive protein-water and protein-cosolvent interactions that would further help us to know whether the cosolvent governed phenomenon follows the direct mechanism or it an indirect interaction in which the presence of cosolvent alters the water properties and hence promotes the respective process.

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Quantum Fokker-Planck equation with positive definiteness condition via path integral influence functional formalism

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Quantum Fokker-Planck equation (QFPE) offers a well-defined way to extend classical Brownian motion for quantum regime, but microscopic derivation of a satisfactory form of QFPE remains challenging. Best known form of QFPE is the one derived long time ago by Caldeira and Leggett (CL) employing the Feynman-Vernon influence functional formalism. While this CL-QFPE has served as a key theory for a wide range of condensed phase quantum dynamical processes and for understanding quantum decoherence, its non-positivity has remained an important theoretical issue to be improved upon. This talk presents a recent generalization [1] of the CL-QFPE for photo-induced nonequilibrium processes and for intermediate temperature regime. This is achieved through consistent expansions of the paths of the influence functional up to the second order with respect to time and Gaussian integration complex domain. The resulting equation can account for non-equilibrium effects of the bath through time dependent kernels and additional terms, and has clear positive definiteness condition. The steady state limit of this QFPE also provides corrections of CL-QFPE for the quantum and non-Markovian effects of the bath.

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Nuclear magnetic dipole moments from NMR experiments

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We discuss new values of nuclear magnetic dipole moments, obtained from accurate absolute shielding constants and experimental NMR data, for a series of nuclei. The generally accepted literature values of magnetic moments were for many isotopes derived from NMR spectra. However, in the procedure applied to determine the moments of bare nuclei the effects of the molecular electronic structure have been often described in a very approximate manner. Accurate absolute shielding scales can be presently established analysing NMR spectra and shielding constants determined by ab initio methods of quantum chemistry.

We focus on the ^{209}Bi magnetic moment, which is of importance for the interpretation of Bi^{82+} ion hyperfine splitting experiments. Our values derived from NMR experiment and calculated shielding constants of Bi^{3+} ions in aqueous solutions of Bi(NO$_3$)$_3$ and Bi(ClO$_4$)$_3$ salts differ from old literature data and represent an independent confirmation of ^{209}Bi magnetic moment recently determined. The accuracy limit of the ^{209}Bi magnetic moment set by the present computational chemistry methods is discussed.

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Beyond Scalar Measures: Directional Chemical Perspective with Next Generation QTAIM

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The theoretical chemical physics/bio-chemistry that the BEACON research group undertakes seeks to develop new theory and explanations for chemical observations whilst also posing questions to be answered by future experiments. Our (next generation) QTAIM based research pioneers new theoretical tools that provide a new 3-D vector based perspective to solve what was only until recently considered unsolvable. An example of this was our explanation of chirality using only chemical measures [1]. By providing new tools based on ignoring previous assumptions in theoretical chemistry/chemical physics we can currently address new areas such as isotope separation, excited state dynamics [2], prediction of competitive and non-competitive ring-opening reactions [3], excited state phenomena [4], physical properties including the application of E-fields [5] and spectroscopic response.

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Calculations of three body recombination and dimer product distributions from ultracold atomic collisions

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The three-body physics of ultracold atoms has proven to be a very rich area of theoretical and experimental studies. This talk describes numerical calculations of three-body recombination based on a simple van der Waals model of two- and three-body interactions that is applicable in the near-threshold region [1]. The model uses pairwise additive long-range dispersion potentials cut off at short range to support a small number $1 \leq N \leq 6$ of s-wave bound states. It accurately represents magnetically tunable multispin two-body Feshbach resonance interactions through a simple parameterization based on known resonance parameters. We demonstrate the power of the method by numerical solution of the three-body scattering problem in the adiabatic hyperspherical representation for several quite different 3-body systems. The model gives a qualitatively similar account to measured product distributions of dimer vibrational-rotational states with binding energies up to $E/h = 15$ GHz for recombination of three ultracold ^{87}Rb atoms [2]. The model gives an accurate value for the measured three-body recombination coefficient of three unlike-spin ^{87}Sr fermions held in optical lattice cells with precisely 3-atom occupancy [3]. Finally, we develop a multispin model to compare to recent very precise measurement of the Efimov peak of magnetically tunable three-body recombination near the moderately strong 33.5803(14) G two-body Feshbach resonance of ^{39}K atoms in the $f = 1$, $m_f = -1$ Zeeman state [4]. Our multispin model accurately represents the variation of two-body scattering length with magnetic field for this resonance and predicts an Efimov feature at a scattering length of -13.1 r_{vdW}, where r_{vdW} is the van der Waals length of the two-body potential. Our calculation is in substantially better agreement with the measured value, -14.08(17) r_{vdW} [4], than the prediction, -9.7 r_{vdW}, based on a single-channel model of "van der Waals universality" for cold atomic systems.

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Catalysts Discovery and Understanding with Computational and Data-Driven Approaches

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Novel materials discovery is a key to addressing many challenges in energy, climate change, and future sustainability. Usual procedure of finding innovative materials based mainly on experiments, however, can take far too long due to a vast and discrete search space, and thus accelerating this process by orders of magnitude using scalable computations would significantly reduce the time and cost of new discovery. In achieving this grand goal, density functional first principles simulation offers a sweet spot between the prediction accuracy and feasibility. I will demonstrate some of the examples to discover new materials in energy conversion applications using them. I will also talk about some of our recent efforts to use machine learning for chemical science that can contribute greatly to creating potential solutions to some of these materials problems.

Collisional loss of ultracold molecules

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(Dated: June 23, 2019)

The lifetime of nonreactive ultracold bialkali molecules was thought to be limited by sticky collisions that amplify three-body loss. We show that the sticking times were previously overestimated, and cannot explain the loss. Instead, we consider excitation of long-lived collision complexes by the trapping laser. We show typical excitation rates are two orders of magnitude faster than the dissociation rate. This leads to effective two-body loss, as observed in several experiments. Possible workarounds include the use of longer laser wavelengths, uniform box potentials created with blue-detuned trapping lasers, or shielding from molecular collisions.

Shielding may be achieved using microwaves that induce repulsive long-range interactions between ultracold polar molecules. The resulting shielding suppresses various loss mechanisms and provides large elastic cross sections. Hyperfine interactions limit the shielding under realistic conditions, but can be suppressed using a modest magnetic field.

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Computational modelling of cellulose and its modifications

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Cellulose is the most common organic polymer on planet earth. It is produced by a wide range of organism including algae, bacteria and plants, the latter being the most known one as plant-based cellulose is used to produce paper products. Our focus is on bacterial cellulose and its modifications for applications in wound dressings and in biomineralization for artificial joints and bone.

To study these issues, we have performed computer simulations of membrane-cellulose systems using phosphatidylcholine and phosphatidylethanolamine lipids [1] and phophorylate cellulose [2]. In the case of membrane-cellulose systems, hydrogen bonds turned out to be the key player. This is, however, not a simple matter as there is a subtle balance between lipid-cellulose and cellulose-water hydrogen bonds. One of the aims to modify cellulose using common polymers such as polylactic acid [3,4] and I will address some of those issues in this talk.

I will also discuss some difficulties in modelling cellulose in the presence of ions. Significant overbinding of sodium ions was observed independent of the force field. To investigate this further, we set up simpler model systems consisting of poly-α,L-glutamic and poly-α,L-aspartic amino acid and studied the interactions between sodium and potassium ions and the amino acids using several force fields and the so-called NBFIX (non-bonded fix) and ECC (electric continuum) corrections.

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Understanding H_2 Formation on hydroxylated nanopyroxene clusters : *Ab initio* Study of the Reaction Energetics and Kinetics

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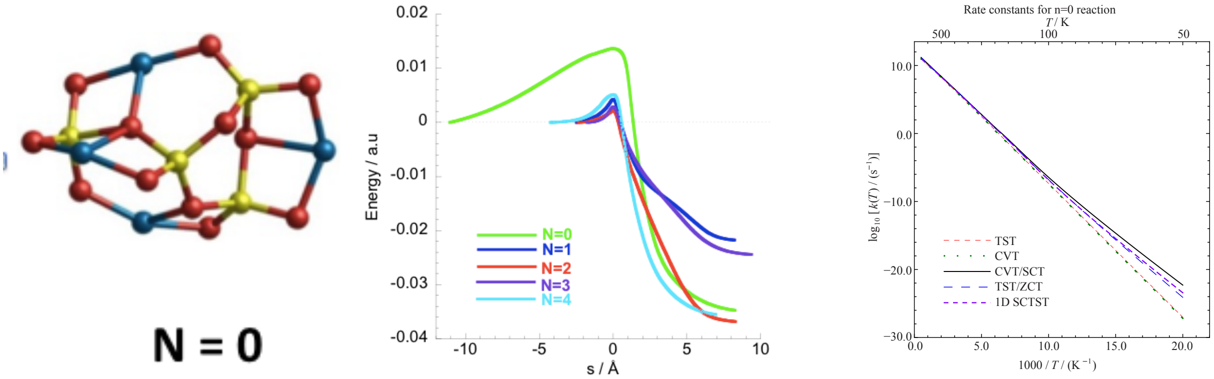
The rate constants of H_2 formation on five models of silicate nanoclusters [1] with varying degrees of hydroxylation $(Mg_4Si_4O_{12})(H_2O)_N$ were computed for a wide temperature range [50-2000K]. We tested the efficiency of nine combinations of density functional methods and basis sets in reproducing accurate reaction energies and barrier heights, and computed the minimum energy $H + H \rightarrow H_2$ reaction paths on each nanocluster. The convergence of the energetic data shows a preference for the largest basis set tested in combination with the hybrid-meta GGA functional M05-2X. The computation of the rate constants employed three semi-classical approaches that take into account tunneling and non-classical reflection effects by means of the canonical variational transition state theory with small curvature tunneling (CVT/SCT) corrections when possible [2], ZCT and the 1D Small Curvature Transition State Theory (SCTST) methods [3], which provided comparable results. Our investigations show that the H_2 process formation following the Langmuir-Hinshelwood (LH) mechanism is more efficient on the hydroxylated (N = 1 - 4) nanoclusters than on the bare (N = 0) one due to the barrier height being higher than for the hydroxylated nanoclusters. Overall, we conclude that all the considered nanoclusters are very efficient catalyzing grains for H_2 formation in the physical conditions of the Interstellar Medium (ISM) with pyroxene nanosilicates having moderate to high hydroxylation being more efficient than bare nanograins.

Figure 1: Logarithmic plot of the calculated reaction rate constants for the N=0 reaction.



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Efficient hybrid density functional calculations in real-space numerical grid methods

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Abstract:

Density functional theory (DFT) has been an essential tool for electronic structure calculations in various fields. In particular, its hybrid method including the Hartree–Fock (HF) exchange term remarkably improves the reliability of DFT for chemical applications and computational material design. However, the conventional hybrid DFT is inefficient for numerical grid-based methods as well as plane-wave-based ones. There are two different types of exchange–correlation potential that can be derived from hybrid functionals. In conventional approaches, the HF exchange operator is adopted as a part of Kohn-Sham (KS) potential. On the other hand, the optimized effective potential (OEP) method provides another way to incorporate the exact exchange in a mean field picture by constructing a local potential from the non-local HF exchange energy. Thus, one may construct a local version of HF that is equivalent to the exchange-only OEP KS-DFT. It has been known that the exchange-only OEP KS theory gives similar occupied orbitals to HF, while its virtual orbitals are different from those of HF.[1,2,3] Therefore, it is expected that an OEP-hybrid method will give similar results for ground state properties with those of the HF hybrid, but different properties for excited state properties.

Here, we show that such a local multiplicative potential can be derived from existing global hybrid functionals using the OEP method.[4,5] We investigate its accuracy for molecules. Furthermore, we find that the new approach enormously accelerates computational speed of grid-based methods compared to the conventional one, which is desirable for large-scale calculations.

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Quantum effects in cold and controlled molecular dynamics

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I will discuss three examples of molecular dynamics where quantum effects are particularly pronounced. (i) The wave nature of matter emerges in cold collisions, giving rise to quantum scattering resonances. Probing these with rotationally state-selected molecules allows for disentangling the isotropic and anisotropic contributions to the inter-particle interaction [1]. (ii) The wave nature of matter also gives rise to phase protection of Fano-Feshbach resonances. I will discuss how this mechanism may protect a bound state from decay despite resonant coupling to a scattering continuum. For rare gas diatomic ions, the corresponding phase dependence results in predissociation lifetimes spanning four orders of magnitude which we find to be in good agreement with experimental measurements [2]. (iii) Yet another signature of quantum mechanics is found in selection rules governing the light-matter interaction. A particularly striking effect is the so-called photoelectron circular dichroism (PECD) found in randomly oriented chiral molecules. I will present a simple, but first principles-based model that allows to explain the PECD that was observed experimentally in the resonantly enhanced multiphoton photoionization of camphor and fenchone molecules [3] and discuss prospects for quantum control [4].

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Computing molecular properties in multireference coupled-cluster theory

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In single-reference coupled-cluster theory the computation of molecular properties builds on two intimately related and now well-established formalisms: Gradient theory [1] and response theory [2]. Here, I want to report on our progress in using these approaches within the framework of internally contracted multireference coupled-cluster (icMRCC) theory [3] with the aim of applying the theory to questions beyond molecular energies.

In one line of our work, we apply the quasi-energy response formalism to icMRCC theory. The approach gives access to excitation energies [4], expectation values [5], and static and dynamic response functions [6]. We will in particular discuss the application to hyperfine coupling tensors [5] and outline some of the subtle problems that occur in the computation of icMRCC response functions [6].

A second thread starts from the multistate generalization of icMRCC theory [7] and focusses on the computation of properties for (quasi-)degenerate states. In particular we will discuss some initial results for the computation of spin-orbit coupling matrix elements of $^2\Pi$ radicals [8].

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Polarizable Density Embedding for Proteins: Excited States in Complex Environments

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In this talk I will review recent progress within the polarizable embedding (PE) and polarizable density embedding (PDE) methods [1-8]. These computational models have both been developed with the aim of enabling calculations of general molecular response properties for large and complex systems, *e.g.* proteins. The PE model builds on the concepts from mixed quantum mechanics / molecular mechanics (QM/MM) schemes, whereas the PDE model is an extension and is formulated within the general framework of QM/QM/MM models. Both models thus represent focused models in which different parts of a large molecular system are described using different levels of approximations. A key concept associated with the PE/PDE models is the introduction of quantum mechanical response theory in combination with polarizable force fields (in PE). This allows for calculation and simulation of general molecular properties, *i.e.* properties relevant for optical and magnetic spectroscopies. We will discuss some recent applications of the PE/PDE models aimed at elucidating optical and magnetic properties of both solute-solvent and heterogeneous molecular systems highlighting the general flexibility and accuracy of this computational model. Finally, we will show how the PDE model recently has been extended to the case of covalently bonded environments, *e.g.* proteins.

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On the Applicability of Various Partitioning Schemes to Intermolecular Interactions

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An availability of partitioning schemes for molecular energies and properties increases considerably the explanatory and predictive power of computational chemistry. Such schemes, although often not strict, are nevertheless physically convincing and allow in many cases to answer important practical questions, concerning e.g. the substituent dependence of stability and reactivity. Some of these partitioning schemes were designed especially for intermolecular interactions, like F-SAPT approach [1], while for other methods the intermolecular interactions are treated on the same footing as e.g. covalent ones (quantum theory of atoms-in-molecules – QTAIM [2], interacting-quantum atoms – IQA [3], etc.). Yet another philosophy stays below the Molecular Fragmentation (MF) models (see e.g. the Systematic MF from [4]), which can also be applied to calculate and to partition intermolecular interaction energy. Here we present a study of suitability of these methods to explain the nature of intermolecular interactions and its dependence on a detailed molecular structure for several nontrivial test cases, like complexes with boron/nitrogen doped analogs of benzene [5] or complexes with calixarenes [6].

Acknowledgements:
This research was supported in part by PL-Grid Infrastructure. The support from the National Science Centre of Poland through grant 2015/19/B/ST4/01812 is gratefully acknowledged.

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Nonadiabatic Transitions via Conical Intersections in Ultracold Chemical Reactions

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Collisions and reactions among atoms, ions and small molecules can now be investigated at temperatures well below 1 mK. Here, quantum effects, such as threshold phenomena, can not be ignored. In this presentation, I will discuss our recent results on ultracold atom-molecule reactivity, focussing on heteronuclear polar molecules, where intermediate short-range complexes with conical intersections are important. Conical intersections correspond to geometries where two potential energy surfaces touch. Nonadiabatic passage through these intersections causes a breakdown of the Born-Oppenheimer approximation that strongly affects molecular dynamics and the chemical properties of molecules. I will also discuss control of ultracold charge exchange among an atom and an atomic ion in the presence of a strong cw laser field. The laser induces a conical intersection and strong non-adiabatic transitions.

Our simulations have required us to perform electronic structure calculations of the multi-dimensional potential energy surfaces of ground and excited states for both short- and long-range internuclear geometries. We located and determined properties of CIs as well as extracted the three-body non-additive contribution to the potentials. We also performed coupled-channels computations based on a first-principles description of the collisional dynamics and determined total reaction rate coefficients as well state-to-state resolved product distributions. We interpret the outcomes in terms of random matrix theory.

Lecture: Lec-105

Transition metal catalyst discovery with high-throughput screening and machine learning

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Computational chemistry has emerged as a leading tool for exploring large regions of chemical space, but many outstanding challenges remain to go from a feasible space to lead compounds that achieve a goal. This challenge is particularly daunting for the design of transition metal complexes due to the combinatorial challenges associated with their variable spin, oxidation state, and coordination number. At the same time, transition metal catalysis, especially at open shell transition metal complexes, represents one of the most fertile regions to explore with such computational techniques. I will describe our recent efforts in automation, high-throughput screening, and machine learning for the discovery of both selective catalysts and design rules. I will talk about how these approaches have allowed us to both identify new scaling relations in catalysis as well as ways to break those scaling relations. Such approaches are expected to enable the discovery and design of selective and active catalysts for challenging transformations (e.g., selective C-H activation). I will also describe our development of representations uniquely tailored for transition metal complex properties and how we obtain not just accurate predictions with machine learning models but also develop new chemical insights. Time permitting, I will describe our next steps in developing artificial intelligence engines that automate decisions that typically require advanced training to determine also when and how to carry out simulations.

Water at electrified graphene interfaces: structure, dynamics, vibrational SFG spectroscopy and consequences for electron transfer reactions

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Water's properties at electrified interfaces are central in e.g. electrochemistry. We will present the main results of our theoretical study of liquid water/electrified semi-metallic graphene sheet interfaces. We find that – surprisingly – the interfacial water molecules' spatial structural and dynamical properties vary non-monotonically with the applied potential. We show that this behavior can be directly understood within the extended jump-model of water hydrogen-bond exchanges. We also indicate how simulated vibrational sum-frequency generation spectra of the water OH stretch depend on the contributions from the interfacial and the subsequent water layers. Finally, several key consequences for interfacial electron transfer reactions are discussed.

On the calculation of quantum mechanical electron transfer rates

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We present a simple interpolation formula for the rate of an electron transfer reaction as a function of the electronic coupling strength. The formula only requires the calculation of Fermi Golden Rule and Born-Oppenheimer rates and so can be combined with any methods that are able to calculate these rates. We first demonstrate the accuracy of the formula by applying it to a one dimensional scattering problem for which the exact quantum mechanical, Fermi Golden Rule, and Born-Oppenheimer rates are straightforward to evaluate. We then describe how the formula can be combined with the Wolynes theory approximation to the Golden Rule rate [1], and the ring polymer molecular dynamics (RPMD) approximation to the Born-Oppenheimer rate [2], to capture the effects of nuclear tunnelling, zero point energy, and solvent friction on condensed phase electron transfer reactions. Comparison with exact hierarchical equations of motion (HEOM) [3] results for a demanding set of spin-boson models shows that the interpolation formula has an error comparable to that of RPMD rate theory in the adiabatic limit, and that of Wolynes theory in non-adiabatic limit, and is therefore as accurate as any method could possibly be that attempts to generalise these methods to arbitrary electronic coupling strengths.

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Attosecond electron dynamics via tensor network state methods in strongly correlated molecular systems

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Quantum many-body systems out of equilibrium pose some of the most intriguing questions in physics and chemistry. Unfortunately, numerically keeping track of time evolution of states under Hamiltonian dynamics constitutes a severe challenge for all known methods. Prominently, tensor network methods are marred by an entanglement blowup, which allows simulating systems following global quenches only to constant time. We present a novel scheme that allows to significantly extend the simulation time for interacting fermionic or equivalent spin systems. We show that if the manifold containing both tensor network states and fermionic mode transformations is chosen, significantly longer times can be achieved. First, we overview general tensor network state techniques, which can be used for the treatment of strongly correlated molecular systems, and connect them to concepts already used in many-body quantum physics. Recent developments on the externally corrected coupled cluster density matrix renormalization group (DMRG-TCCSD) method, fermionic orbital optimization, and time-dependent variational principle (TDVP) will be discussed in more detail. In fact, these are key ingredients of novel algorithms to study dynamics of the electron systems via tensor product approximation. Finally, new results will be shown for extended periodic systems, transition metal complexes, and Wigner crystals.

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Generalized energy-based fragmentation approach for large molecules and condensed phase systems

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In this talk, I will report recent developments and applications of the generalized energy-based fragmentation approach (GEBF) developed by our group for large molecules and condensed phase systems. The GEBF approach is a linear scaling technique that allows ab initio ground-state calculations feasible to very large systems and condensed phase systems at ordinary workstations. Within this approach, the ground-state energy (or properties) of a large molecule can be evaluated directly from the corresponding quantities of various "electronically embedded" subsystems.[1] The GEBF approach has been established to be an efficient and reliable theoretical tool for investigating structures, relative stability, and properties of various complex systems.[2-5] With specifically designed fragmentation schemes, the GEBF approach can be extended to treat metal-containing large supramolecular coordination complexes and ionic-liquid systems.[6-7] The periodic version of the GEBF approach for systems with periodic boundary conditions (PBC-GEBF) has also been established.[8] The PBC-GEBF approach has been employed to obtain the optimized crystal structures and vibrational frequencies of molecular crystals.[9] Our applications demonstrate that the PBC-GEBF method, combined with advanced electronic structure methods, is capable of providing accurate descriptions on the lattice energies, structures, vibrational and NMR spectra for various types of molecular crystals.[10]

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Spin-Orbit Symmetry Breaking and Restoring in Kramers-Unrestricted Multireference Approaches

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The accurate description of the electronic structure of transition metals, heavy-elements, and their compounds can be complicated by both the large number of close-lying states that often have multi-configurational nature in addition to significant relativistic effects. In order to address these challenges we present a Kramers-unrestricted relativistic two-component complete-active-space self-consistent field method (CASSCF) and a multireference configuration interaction (MRCI) that includes scalar relativistic effects and one-electron spin-orbit coupling during the self-consistent wave function optimization procedure. These relativistic effects are included via an "exact two-component" transformation of the solution of the one-electron modified Dirac equation. This approach is variational in nature, allowing the orbitals to be affected by the spin-orbit coupling; a requirement for accurate description of atomic spin-orbit splittings. The ability to restore spin-orbit symmetry/degeneracy in Kramers-unrestricted multireference approaches will be discussed. The qualitative behavior of the methods is highlighted by an example of spin-orbit splitting – the sodium '*d*-line'. The correct spin-orbit splitting structure is restored by optimizing the orbitals using state averaging or using a large active space. The methods are also tests with benchmark calculations of the ground and excited state spin-orbit splitting of lower *p*- and *d*-block elements, as well as some heavy-elements, compared to experiments. The formulation developed in this work is for the general Kramers-unrestricted case, and could be extended to include magnetic field effects in the future, where time-reversal symmetry is no longer preserved.

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Simulations of Ion Solvation and Transfer by Adaptive-Partitioning QM/MM Dynamics

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Ion solvation and transport is important to many physical, organic, and biochemical processes. However, the frequent exchange of solvent molecules between the ion's solvation shell and the bulk solvent presents a challenge for combined quantum-mechanics/molecular mechanics (QM/MM) simulations. Adaptive-partitioning QM/MM allows on-the-fly reclassification of atoms as QM or MM both continuously and smoothly.[1] This permits the use of a small, mobile QM subsystem, with contents that are updated as needed when the trajectory is propagated. In this talk, we report our latest progress in the development of adaptive-partitioning QM/MM strategies (Fig. 1) for simulations of proton transfer through a prototypical chloride/proton antiporter.[2]

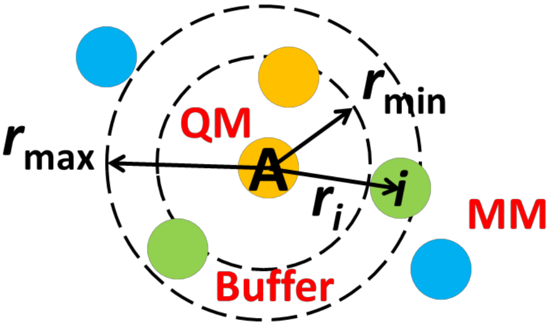

Fig 1. Schematic of adaptive-partitioning QM/MM. The QM zone is centred at a selected molecule or ion A. The distance r_i between a buffer group i and the QM-zone centre satisfies $r_{\max} \geq r_i \geq r_{\min}$. The QM, buffer, and MM groups are coloured in orange, green, and blue, respectively.

Acknowledgement: This work is supported by the NSF (CHE-1564349), Camille & Henry Dreyfus Foundation (TH-14-028), Research Corporation for Advancement (25793), and NVIDIA Corporation. This work used XSEDE under grant CHE-140070, supported by NSF grant number ACI-1053575.

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A general linear scaling implementation for polarizable embedding methods

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Polarizable QM/MM methods are a powerful strategy to model the effects of the environment on the properties of molecules embedded in a matrix, such as a solvent or a biological system. From a computational point of view, embedding schemes require to compute the electrostatic interactions among the MM sites and between the MM and QM region. The former operation, if performed in a straightforward manner, scales with the square of the number of MM site and can easily become a formidable computational challenge for large systems such as biological macromolecules. The cost of an embedding scheme is further aggravated if distributed multipoles are used instead of point charges and, even more, if the embedding scheme includes mutual polarization. In the latter case, a linear system of equations has to be solved for each given QM density[1].

In order to extend the applicability of (polarizable) embedding schemes to large and very large systems, it is paramount to reduce the computational cost associated with the aforementioned operations. *Mutatis mutandis,* such operations can be always written as the computation of some electrostatic quantity, such as the electrostatic potential or its derivatives, or its contraction with the sources. The computation of electrostatic quantities can be performed with a computational cost that scales linearly with the number of sources if a fast summation technique is used[2].

In this contribution, I will present a completely general implementation of polarizable embedding schemes that achieves linear scaling in computational cost and memory requirements. The implementation relies on the Fast Multipole Method[3] (FMM) to compute the required electrostatic quantities and can handle sources, including polarizable ones, up to the quadrupole. Furthermore, the implementation can handle excluded or scaled interactions between MM sites, as well as damped Coulomb kernels for the polarization interactions. I will show some scaling and timings for the specific case of the AMOEBA force field[4], which treats the electrostatics in terms of distributed charges, dipoles and quadrupoles and polarization via induced dipoles. Nevertheless, the framework can be easily extended to any other polarizable scheme and can also be generalized to arbitrary order multipoles.

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Path integral Liouville dynamics for real time dynamics & a unified framework for path integral molecular dynamics for quantum statistics

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We first show a unified second-order scheme for constructing simple, robust and accurate algorithms for typical thermostats for exact quantum/classical statistics for the canonical ensemble. The scheme consistently improves the efficiency for evaluating all quantum thermodynamic properties for any type of thermostat. Even when the Born-Oppenheimer approximation is broken, the unified scheme offers a powerful and accurate tool for studying non-adiabatic systems in thermal equilibrium.

In the second part of the talk, we show a new imaginary time path integral based method—path integral Liouville dynamics (PILD) in the Wigner phase space. PILD offers a potentially useful approach for molecular systems to have the two important properties: conserves the quantum canonical distribution and recovers exact thermal correlation functions (of even nonlinear operators, i.e., nonlinear functions of position or momentum operators) in the classical, high temperature, and harmonic limits. Some applications to water, ammonia, methane, zundel cation, and liquid para-hydrogen will be demonstrated.

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Many-electron Correlations in Multi-particle Excitations and Nonlinear Optical Processes in Materials

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Excited-state phenomena in a material typically give rise to its defining attributes and determine its usefulness. These phenomena are particularly important in processes of energy conversion, transport and storage. However, *ab initio* methods for them - especially for correlated multiple-particle (3- or 4-particle) excitations, nonlinear optical processes, and electron dynamics including relevant electron-electron interactions - have been under-explored and hence limiting their studies for real materials. In this talk, we report recent progress on the *ab initio* theory and computation of such excited-state phenomena based on the interacting Green's functions approach to many-body perturbation theory. We present: 1) our new formalism and computational method for 3- and 4-particle correlated excitations with applications to trions and biexcitons in reduced-dimensional materials; and 2) our development of a time-dependent GW approach for time-dependent processes and nonlinear optics, which has led to the discovery of giant exciton effects in shift currents in two-dimensional semiconducting materials.

Recent developments in dynamic spectroscopic methods for the gas and condensed phase

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Spectroscopy is an indispensable tool for the analysis of compounds. Calculations provide valuable insight and allow the targeted study of specific structures, their dynamics and interactions.

We present innovative methods for the calculation of spectroscopic signatures based on real time propagation as well as density functional theory-based molecular dynamics (DFT-MD) with a focus on vibrational spectroscopy. Besides the study of solvation effects [1,2,3], efficient DFT-MD approaches for Infrared and Raman spectroscopy for condensed phase systems [4,5], relying e.g. on periodic subsystem density functional theory [4], have been presented. Other developments have dealt with DFT-MD for Sum Frequency Generation and Raman Optical Activity spectroscopy [6,7]. Moreover, innovative analysis methods have been presented [4,5,8]. This has paved the way for the computationally efficient and accurate study of molecules on (semiconductor) surfaces/interfaces and in gas/liquid phase at ambient conditions with consideration of anharmonicity and realistic band shapes in the spectra. Among various investigated systems, chiral ionic liquids have been explored in detail [9]. Another direction has concerned the use of real time propagation for linear spectroscopy and excitation profiles in vibrational spectroscopy [10].

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Systematic Generation and Analysis of Reaction Path Networks by the Artificial Force Induced Reaction Method

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Paths of chemical reactions are studied theoretically by exploring the potential energy surface (PES) while performing quantum chemical calculations. Equilibrium (EQ) structures of molecules and transition state (TS) structures of chemical reactions are computed as local minima and first-order saddle points on the PES. Therefore, development of a method for finding EQs and TSs systematically is an important subject.

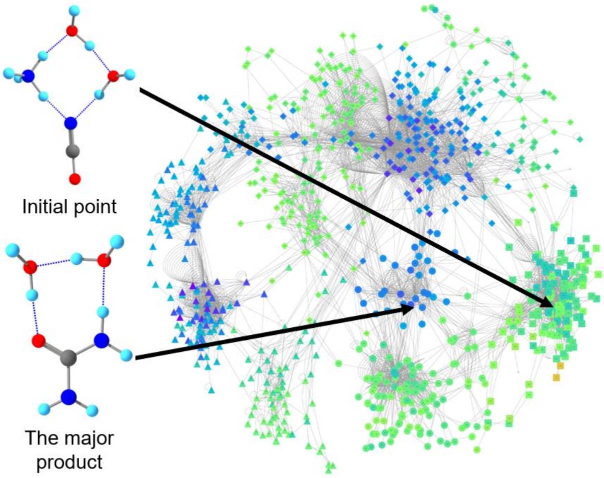

Figure 1. A reaction path network for Wöhler's urea synthesis [5].

We have developed an automated reaction path search method called an artificial force induced reaction (AFIR) method [1]. It has been used to elucidate mechanisms of various organic reactions [2]. The AFIR method has been implemented in the global reaction route mapping (GRRM) program, where the AFIR method for molecular systems is available in GRRM17 [3].

The AFIR method can generate a network of reaction paths. The resultant reaction path networks contain hundreds or more EQs. We have developed a kinetic theory called a rate constant matrix contraction (RCMC) method which is applicable to huge reaction path networks [4]. Furthermore, by combining the AFIR method with the RCMC method, we have established an approach by which, starting from a set of reactants and catalysts, the product and all byproducts, their generation ratio, as well as their generation mechanisms can be elucidated automatically [5]. This approach enabled systematic prediction of chemical reactions. In the presentation, its applicability and limitation will be discussed.

The AFIR method itself is applicable to chemical reactions of various types such as photoreactions, enzyme reactions, reactions on metal surfaces, phase transitions, and so on. Application examples to these reactions will also be presented.

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Modular Quantum and Rigorous Quantum-Classical Real-Time Path Integral Methods

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The quantum-classical path integral (QCPI) offers a rigorous, yet efficient methodology for combining a quantum mechanical description of a target “system” with a classical trajectory treatment of the system’s environment, which is often composed of thousands of atoms.[1-4] Real-time path integral methods are plagued by the Monte Carlo sign problem, while explicit summation of all the terms is not feasible in most situations, as the number of quantum paths grows exponentially with the number of time steps. Since in QCPI each quantum path specifies a sequence of forces that generate a different classical trajectory (from the same phase space point), the number of trajectories also grows exponentially with propagation time. Overcoming these problems has been possible by exploiting decoherence.

The starting point is the identification of two components in the effects induced on a quantum system by a polyatomic environment. The first, “classical decoherence” mechanism is associated with phonon absorption and induced emission and is dominant at high temperature. Within the QCPI framework, the memory associated with classical decoherence is removable. A second, nonlocal in time, “quantum decoherence” process, which is associated with spontaneous phonon emission, becomes important at low temperatures and is responsible for detailed balance.[5] The QCPI methodology takes advantage of the memory-free nature of system-independent solvent trajectories to account for all classical decoherence effects on the dynamics of the quantum system in an inexpensive fashion. Inclusion of the residual quantum decoherence is accomplished via phase factors in the path integral expression, which is amenable to large time steps and iterative decompositions. The QCPI methodology can be used to perform all-atom simulations of nonadiabatic processes in condensed phase environments with thousands of atoms [6], without the need for any assumptions (beyond the classical trajectory treatment of the environment) or adjustable parameters.

Further, a modular path integral (MPI) methodology has recently been developed [7,8], which provides an efficient, fully quantum mechanical framework for simulating the dynamics of Hamiltonians characterized by a quasi-one-dimensional topology and mostly local interactions. The MPI decomposition proceeds through sequential linking of the quantum paths corresponding to adjacent monomers, achieving linear scaling with system size. An efficient factorization leads to almost linear scaling with the number of monomer paths. The scheme is applicable to systems with considerable chemical complexity.

The MPI approach allows fully quantum mechanical simulation of spin models, as well as Frenkel exciton chains, where any number of harmonic vibrations (with appropriate discrete frequencies and Huang-Rhys factors) as well as lattice phonons representing dissipative interactions, may be included (at zero or finite temperature) without a significant increase in computational cost [9]. In combination with the QCPI algorithm, the MPI approach may be used to simulate energy transfer dynamics of molecular aggregates containing many vibrational degrees of freedom in contact with anharmonic environments with unprecedented accuracy.

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European Research Council session

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The European Research Council (ERC) is Europe’s leading funding agency supporting excellent and investigator-driven frontier research across all fields of science.

ERC calls are open to applicants from all over the world and provide several outstanding funding opportunities with grant-budgets ranging from 1.5 to 3.5 million euro.
All nationalities are welcome, provided that the projects are carried out at a host institution located in Europe (i.e. European Union Member States or the countries which have associated to the EU research funding programmes).

Since 2007, the ERC has financed more than 370 individual research projects in the field of Physical and Analytical Chemical Sciences (panel PE4)[1].

In this informative session, the main features of the ERC individual grants (i.e. Starting, Consolidator and Advanced Grants) will be presented, together with information on the application and evaluation process.

Two former grantees will share their experiences and will provide advices on relevant aspects of the process, such as identifying a solid idea and writing a successful proposal.
Finally, anybody from the audience will have the chance to ask questions to the speakers.

This ERC session is open to all the attendees of the ISTCP congress and will be particularly helpful to early-career and mid-career participants, especially post-docs, researchers and professors who think about applying for funding to conduct breakthrough-research in Europe.

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[1] Source: *https://erc.europa.eu/projects-figures/statistics*

Path integral methods for reaction rates

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In this talk, I will review both the ring polymer molecular dynamics (RPMD) rate theory approximation to adiabatic (Born-Oppenheimer) reaction rates [1-7], and the Wolynes theory approximation to non-adiabatic (Fermi Golden Rule) reaction rates [8,9]. Both of these theories are based on imaginary time path integrals, both provide an excellent description of quantum mechanical zero point energy and tunnelling effects, and both are readily applicable to chemical reactions in arbitrarily complex (anharmonic and multi-dimensional) systems. My review will serve as an introduction to Joseph Lawrence's talk later in the same session, in which he will show how the RPMD rate theory approximation to the Born-Oppenheimer rate and the Wolynes theory approximation to the Golden Rule rate can be combined to give a highly accurate path integral description of electron transfer rates across the full range of electronic couplings from the non-adiabatic to the adiabatic regime [10].

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Multi-scale approach: a versatile platform for investigating novel two-dimensional-material based device concepts

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It is nowadays more and more urgent to devise a robust and precise modeling framework able to incorporate the different 2D materials and their possible combinations in order to explore their applicability in electronics. In fact, the advent of graphene and related 2D materials has already opened the possibility to boost the transistor performance as well as to conceive novel devices by engineering new materials with tailored properties. By means of a first-principle multi-scale approach we study multiple device configurations for digital applications. The method used is articulated in three steps: density-functional-theory (DFT) calculations [1], then we pass through the expression of the Hamiltonian on the basis of a maximally localized Wannier function [2], which feeds the open-source device simulator NanoTCAD ViDES [3], based on a non-equilibrium Green's-function formalism. Specifically, we assess the performance of transistors based on InSe [3], we present lateral heterostructures made of different phases of monolayer MoS_2 [4] combining metallic and semiconducting phases to build up a Schottky diode and a lateral heterostructure FET. Then we explore different Noble TMDs materials, combining bilayer and monolayer crystals, as building block for nanoscale transistors [6]. Particular attention will be also devoted to Stanene, which has interesting features when cut into zig-zag nanoribbon. We present two different tunnel field effect transistors (TFET) using Stanene nanoribbons: a proposal of a purely one-dimensional channel TFET device [7] and a spin filter which exploits the possibility of independently tune the gap for spin up and spin down carriers with a lateral electric field [8]. Finally we present an example on how theoretical methods can help to experimental device realizations and experimental data interpretation [9].

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Accurate and Efficient Non-adiabatic Quantum Dynamics using Master Equations

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The exact treatment of real time nonadiabatic quantum dynamics in condensed phase chemical systems remains a significant challenge that spurs the ongoing development of approximate methods that are accurate, efficient, and can treat large systems with a wide range of different forms of interactions. Quantum-classical trajectory based methods provide some of the most appealing solutions to this problem that offer a hierarchy of approaches with different balances between accuracy and computational cost. However, since moving up this hierarchy typically requires orders of magnitude more computational effort, only the lowest tiers are likely to be practical, both now and in the foreseeable future, for nonadiabatic problems containing large quantum subsystems. In this talk I will discuss our recent research showing both how and why quantum-classical approaches can be made both more accurate and efficient by combining them with the formally exact quantum master equation framework. This combination of quantum-classical theory and master equation techniques makes it possible to obtain the accuracy of much more computationally expensive approaches at a cost an order of magnitude faster than even the most efficient trajectory based approaches, providing the ability to treat the quantum dynamics of atomistic condensed phase systems for long times.

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Attosecond pump-probe spectroscopy of molecular electron dynamics

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Attosecond light pulses allow one to probe the inner workings of atoms, molecules and surfaces on the timescale of the electronic motion. In molecules, sudden ionization by an attosecond pulse is followed by charge redistribution on a time scale from a few-femtoseconds down to hundreds attoseconds, which is usually followed by fragmentation of the remaining molecular cation. Such complex dynamics arises from the coherent superposition of electronic states covered by the broadband attosecond pulse and from rearrangements in the electronic structure of the molecular cation due to electron correlation. To investigate these ultrafast processes, attosecond pump-probe and transient absorption spectroscopies have been shown to be very valuable tools [1-8]. In this talk I will present the results of molecular attosecond pump-probe theoretical simulations in which several molecules, from the simplest H_2 one to the aminoacids phenylalanine and tryptophan, are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. In all cases, the evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions can be inferred from the measured (or calculated) ionization or fragmentation yields with attosecond time-resolution, and can be visualized by varying the delay between the pump and probe pulses. The results of this work will serve as a guide of future experimental efforts in more complicated molecules and may open the door to the control of charge transfer in biologically relevant processes [9].

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Do CCSD and Approximate CCSD-F12 Variants Converge to the Same Basis Set Limits? The Case of Atomization Energies

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Basis set convergence of computed thermochemical properties is dominated by the CCSD contribution: (T) converges considerably faster [1], while higher-order correlation effects converge ever more rapidly as one ascends the coupled cluster hierarchy [2]. Approximate CCSD-F12 methods offer greatly accelerated basis set convergence over conventional CCSD. From purely theoretical arguments, CCSD and CCSD-F12 without approximations must converge to the basis set limit; however, the truth is more complicated for *approximate* F12 methods and *practical-sized finite* (one-particle) basis sets. To shed further light on this issue, the convergence to the basis set limit of CCSD (coupled cluster theory with all single and double excitations) and of different approximate implementations of CCSD-F12 (explicitly correlated CCSD) has been investigated in detail[3] for the W4-17 thermochemical benchmark[4]. $L \leq 7$ was considered in the conventional, and $L \leq 5$ in the explicitly correlated calculations. Near the CBS ([1-particle] complete basis set) limit, CCSD and CCSD(F12∗) agree to within their respective uncertainties due to residual basis set incompleteness error (about ±0.04 kcal/mol), but a nontrivial difference remains between CCSD(F12∗) and the popular CCSD-F12b model even for basis sets as large as cc-pV5Z-F12 [5]. Said difference is roughly proportional to the degree of static correlation as gauged by various diagnostics. Combining empirical observations with an earlier multiple perturbation analysis[6], we learn that the observed basis set convergence behavior results from the superposition of a rapidly converging, attractive, CCSD[F12]–CCSD-F12b difference (consisting mostly of third-order terms) and a more slowly converging, repulsive, fourth-order difference between CCSD(F12∗) and CCSD[F12]. For accurate thermochemistry, we recommend CCSD(F12∗) over CCSD-F12b if at all possible. There are some indications that the nZaPa family of basis sets[7] exhibits somewhat smoother convergence than the correlation consistent family.

As a by-product, we obtain a slight revision of the W4-17 reference values.

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Potential Energy Surfaces and Nonadiabatic Dynamics in Photoactive Proteins from First Principles

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We discuss new efficient and accurate approaches for the computation of excitation energies and nonadiabatic dynamics in proteins, including both static and dynamic electron correlation. A graphical processing unit (GPU)-based implementation of the tensor hypercontracted XMS-CASPT2 method is described, enabling computations of excitation energies for hundreds of quantum mechanically-treated atoms (and further including thousands to tens of thousands of surrounding atoms treated by an empirical force field).[1,2] We also describe our GPU-based implementation of the state-interaction/state-averaged restricted ensemble Kohn-Sham (SI-SA-REKS) method.[3,4] We compare the performance and accuracy of this method to conventional XMS-CASPT2 and show that SI-SA-REKS can provide XMS-CASPT2 accuracy at a cost which is nearly that of ground state DFT. We apply the SI-SA-REKS method in combination with ab initio multiple spawning to the nonadiabatic dynamics of channelrhodopsin-2,[5,6] a protein which has seen wide use in optogenetics.

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Ultra-precise computations for molecular paradigms

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I report on recent developments and applications about the coupled quantum mechanical motion of the electrons and the atomic nuclei through a variational [1] and also a perturbative [2] approach. For the applications, the underlying Schrödinger equation is solved using a symmetry-adapted, explicitly correlated Gaussian ansatz. The variational, pre-Born–Oppenheimer, approach has been extended towards (a) the solution of H_3^+ as an explicit five-particle problem [3], and (b) tightly converged electronically excited, rovibronic states of the H_2 molecule which appear as resonances in the full electron-nucleus problem [4]. Concerning the perturbative route to small non-adiabatic effects, we have formulated the second- (and third-)order effective Hamiltonian for the quantum nuclear motion over coupled electronic states containing diagonal and off-diagonal non-adiabatic mass-correction terms [2]. The general curvilinear expression for the non-adiabatic kinetic energy (mass) correction has been formulated [5] and its numerical properties have been studied for selected examples [6]. The non-adiabatic correction to the nuclear mass usually amounts to ca. the mass of the electrons, but for special examples non-trivial deviations arise. For example, in the outer-well of the $H\bar{H}\ {}^1\Sigma_\mathrm{g}^+$ electronic state of H_2, the dressed, vibrating proton is lighter than the proton itself, which accounts for part of the discrepancy of experiment and theory [7]. In order to achieve quantitative agreement between the computations and high-resolution spectroscopy experiments, it is necessary to account also for relativistic and radiative effects, for which we evaluate perturbative corrections for the non-relativistic result. Our recently computed pre-Born–Oppenheimer term values for the rotationally excited $EF\ {}^1\Sigma_\mathrm{g}^+$ states of H_2 $(N = 0, 1, \ldots, 5)$ [4], appended with relativistic, leading- and higher-order radiative corrections, are in a $0.001 \pm 0.005\ \mathrm{cm}^{-1}$ agreement with experiment [8]. Further improvement of the theoretical uncertainty should reveal fine details of higher-order radiative corrections and the finite size of the proton.

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The protein is the key: the unique chemistry of biological pigments revealed by a multiscale strategy

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Molecular pigments behave differently when they are embedded in a protein. The electrostatic fields acting in the protein cavity and the (mutual) interactions with the nearby residues can in fact largely affect the nature and the relative energy of pigments' electronic states. Moreover, their conformational space and vibrational motions can be strongly modified. All these effects finally lead to a new chemistry which is at the basis of some of the most important biological functions. The molecular mechanisms determining such a new behavior can only be revealed by computational approaches which are able to couple the structural, electronic and dynamic properties of the pigments and the embedding protein. In this talk, examples of this multiscale modeling will be discussed for biological pigments present in plants and bacteria.

Towards an improved understanding of interfacial water

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In this talk I will discuss some of our recent work related to water and ice at surfaces. This will include new insights into the structure of interfacial and confined water as well as the role nuclear quantum effects play in such systems.

Modeling reactivity at the catalyst/water interface

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To describe reactions occurring at the solid/water interface is currently one of the major challenges in modeling in Heterogeneous Catalysis, especially in the context of biomass valorization.[1] It requires a proper depiction of the water solvent together with an adequate description of the surface state. Several approaches are available nowadays in the literature, from continuum models to a full explicit description of the liquid water.[2] When H-bonding between the liquid water and the reactant or intermediate is crucial, continuum models are not sufficient and an explicit inclusion of water molecule is a necessity. As a first step, micro-solvation can be an effective approach that allowed us to interpret solvent effect in the conversion of levulinic acid into γ-valerolactone.[3] Moving to a full description of reactivity the water/metal interface is still beyond a full complete DFT approach provided the minimal size of the periodic cell that is necessary and the minimal sampling required. A combined QM/MM approach could be a promising strategy,[4] but necessitates a new generation of metal/water force field.[5] Nevertheless, being less demanding, inspecting transformations occurring at oxide/water interface is now reachable, as illustrated by our recent work on the stability of γ-alumina in water. After a fine characterization of the interfacial water[6], we located the weak spot on γ-alumina by a combination of experimental reactivity of shaped-controlled crystals and metadynamics simulations and finally provided a rational for the greatest stability in presence of C5 and C6 polyols.[7]

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Classical and Machine-Learning Methods for Quantum Simulation

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A focus of our research is to the develop simulation methods that reveal the mechanistic details of quantum mechanical reactions that are central to biological, molecular, and heterogenous catalysis. The nature of this effort is three-fold: we combine quantum statistical mechanics and semiclassical dynamics methods to expand the scope and reliability of condensed-phase quantum dynamics simulation; we develop quantum embedding and machine learning methods that improve the description of molecular interactions and electronic properties; and we apply these methods to understand complex chemical systems.

The talk will focus on recent developments [1] and applications of Feynman path integral methods for the description of non-adiabatic chemical dynamics, including long-ranged electron transfer in proteins [2] and atom-surface collisions [3]. Additionally, we will describe a machine-learning approach [4,5] to predicting the electronic structure results on the basis of simple molecular orbitals properties, yielding striking accuracy and transferability across chemical systems at low computational cost.

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Can we derive many-body non-additive polarization energies from 1-body properties and 2-body energies only?

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Force-fields are normally fitted to a range of data, which could be experimental or theoretical, or a mixture of both. As a rule, many-body intermolecular interaction models are fitted to a range of energies computed on dimers, trimers and often even larger clusters of the interacting molecules. This is done so as to get a good representation of the many-body interactions in the system, but while it is possible to make such extensive computations on small systems like water, it is not generally feasible on larger systems. So we raise the question: Can we derive the many-body polarization energies from molecular properties and a dimer energy evaluations only?

Using very recent work on water models [1] we demonstrate that this is indeed possible. Central to this scheme are the distributed molecular multipoles computed using the basis-space implementation of the iterated stockholder atoms (BS-ISA) algorithm [2], the distributed molecular polarizabilities computed using the ISA-Pol algorithm [3], and charge-delocalization energies defined using regularized-SAPT(DFT) [4]. With these ISA-based molecular properties and a limited number of SAPT(DFT) and regularized-SAPT(DFT) interaction energies computed on dimers only, we can now construct accurate many-body interaction models that correctly describe many-body polarization effects. Using a series of water models of varying complexity we demonstrate how these DIFF (derived intermolecular force fields) models are very close to optimal and have a remarkable predictive power for both the energerics and geometries of large water clusters.

All of the techniques described in this talk are available in the CamCASP code [5] and more information can be found on the CamCASP wiki.

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Linear-scaling DFT simulations of complex nano-structured materials using the CONQUEST code

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First-principles simulations based on the density functional theory (DFT) are powerful tools to clarify the structural and physical properties of various materials at atomic scale. However, usual DFT methods cannot treat complex and large systems containing many thousands of atoms, since the calculation cost increases very rapidly, proportional to the cube of the number of atoms N in the system. To overcome this size limitation, we developed a linear-scaling, or O(N), DFT code CONQUEST. The code is based on the local orbital method and uses a density matrix minimization method to achieve the O(N) behavior. Using the code, we can treat large and complex systems containing more than 100,000+ atoms. We are planning to open the code with the MIT license soon.

In this talk, we will give an overview of the calculation methods used in the code, with its parallel efficiency on massively parallel computers. Then, we will present our recent study of nano-scale materials, Si/Ge or Ge/Si core-shell nanowires. We will show that CONQUEST can calculate the strain distributions in the actual size of the nanowires created experimentally, and unique electronic structure of Si/Ge or Ge/Si core-shell nanowires will be discussed. Some other applications using first-principles molecular dynamics will be also introduced.

This work was done in collaboration with Dr. J. Lin (NIMS) and Prof. D. R. Bowler (UCL). The code is developed jointly by the groups of University College London (D. R. Bowler), NIMS (TM, A. Nakata, Z. Raza, J. Lin, S. Yadav), and the University of Bordeaux (L. Truflandier). This work was supported by World Premier International Research Center Initiative (WPI Initiative) on Materials Nanoarchitectonics (MANA), New Energy and Industrial Technology Development Organization of Japan (NEDO) Grant (P16010), "Exploratory Challenge on Post-K computer" by MEXT, and JSPS Grant-in-Aid for Scientific Research (18H01143).

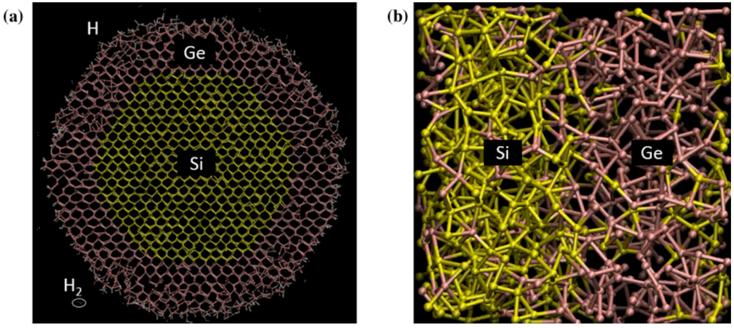

Figure 1: Snapshot structures of linear-scaling first-principles molecular dynamic simulations of Si/Ge core-shell nanowire (Left) and Si/Ge interfaces (Right)

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New physics with ultracold strontium molecules

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State-of-the-art *ab initio* methods of quantum chemistry have found numerous applications in many areas of atomic, molecular, condensed matter, and nuclear physics. During the last decade they have been applied with success to interpret precision experiments on two-body and many-body processes in atomic gases in the ultracold regime. In this talk I will present recent examples of successful applications of the *ab initio* methods to describe two-body processes in atomic optical lattices leading to the formation of unusual chemical bonds, to observations of exotic optical transitions in diatomic molecules [1-3], and to photodissociation processes with the full quantum state control [4-7]. All reported theoretical results will be illustrated by an extensive comparison between theory and experiment.

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Ultrafast spectroscopy and imaging of molecules with classical, quantum, and noisy x-ray pulses

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We demonstrate how stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of the valence electronic state wavepacket created by e.g. photoexcitation, photoionization and Auger processes. Conical intersections (CoIn) dominate the pathways and outcomes of virtually all photophysical and photochemical molecular processes. Short X-ray pulses can directly detect the passage through a CoIn with a high temporal and spectral sensitivity. Applications will also be made for X ray sum frequency generation, and detecting molecular chirality.

Quantum light opens up new avenues for spectroscopy by utilizing parameters of the quantum state of light as novel control knobs and through the variation of photon statistics by coupling to matter. Nonlinear optical signals induced by quantized light fields and entangled photon pairs will be presented. Quantum phase-sensitive diffraction and imaging using entangled photons is presented. A novel quantum diffraction-based far-field imaging technique whereby one photon of an entangled pair is diffracted of a sample and detected in coincidence with its twin is proposed. When a molecule interacts with an external field, the phase information is imprinted in the state of the field in a detectable way. A Schmidt decomposition of the state of the field and the resulting diffraction signal can be used for image enhancement by reweighing the Schmidt modes. Imaging with weak quantum fields is made possible, avoiding damage to delicate biological samples.

Time- and frequency-resolved ultrafast diffraction of noisy X-ray pulses is presented. A frequency-dependent stochastic phase can be used as a frequency marker. Separation of different frequency contributions to the diffraction pattern can be achieved. Fine-tuned correlation functions can control specific charge density contributions. These results are applicable for inherently noisy sources such as SASE free electron lasers, as well as to coherent sources with intentionally added randomness.

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Relativistic density functional theory with picture-change corrected electron density

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Because one-component (1c) relativistic density functional theory (RDFT) can be implemented easily by extending a program code of nonrelativistic(NR) DFT, it is a standard and practical scheme to perform an all-electron calculation including scalar relativistic effects. Although many quantum chemical program packages adopt such 1c DFT approach, the inconsistency of pictures of Hamiltonian and density are involved. Namely, despite the one-electron Dirac Hamiltonian and the two-electron Coulomb operator are transformed to eliminate the small components or to decouple the electronic and positronic components, the electron density, which is the fundamental variable to evaluate the exchange-correlation energy, is obtained by using the NR density operator. We have developed the picture-change corrected (PCC) RDFT that relies on a unitary-transformed density operator as well as a unitary-transformed Hamiltonian [1,2]. Furthermore, we have examined the techniques to reduce the computational cost to evaluate the PCC density. This approach has been implemented into the relativistic program package developed in the author's group, namely, Relativistic And Quantum Electronic Theory (RAQET) [3]. In the presentation, I will explain the theoretical aspects, implementation, and some numerical applications of the present approach.

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Exact Subsystem Time-Dependent Density-Functional Theory

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Frozen-Density Embedding (FDE-) TDDFT [1,2] and subsystem TDDFT [3] are powerful tools to investigate excited states of large systems of molecules in complex environments or chromophore aggregates. Combined with "exact" embedding strategies, accurate results for excitation energies of embedded molecules can be achieved [4,5,6]. Here, we present a new, open-source implementation [6,7] of FDE-TDDFT and subsystem TDDFT that includes (i) a generalization to unrestricted reference orbitals and open-shell cases, (ii) a combination with potential-reconstruction techniques of top-down and bottom-up type, and (iii) a combination with projection-based exact embedding schemes. In connection with the latter topic, we identify an implicit approximation made in Ref. [5] that led to small numerical deviations from reference results and demonstrate that with the correct setup of the response kernel, conventional TDDFT results can exactly be reproduced with subsystem TDDFT even in challenging situations involving covalent bonds between subsystems [8].

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Variational Excited States in DFT, QMC, and Quantum Chemistry

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We will discuss uses for excited state variational principles across a wide range of electronic structure contexts, including mean field theory,[1] density functional theory,[2] multi-reference theory,[3] and quantum Monte Carlo.[4] In all of these areas, variational approaches allow excited states to be modeled without the need for additional approximations beyond those present in the ground state theory. For example, this approach avoids (a) the need for the adiabatic approximation in density functional theory,[2] (b) the need to use ground state orbitals in correlated quantum chemistry methods,[1] and (c) the need for state averaging in multi-reference methods.[3] Remarkably, in all of these cases, the variational excited state approach achieves a cost scaling equivalent to the corresponding ground state method.[1-4] In addition to discussing the formalism behind these developments, we will present preliminary results showing how the removal of common excited state approximations leads to improved predictive power in difficult cases like charge transfer excitations[1,2] and double excitations.[3]

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Attosecond-resolved Quantum Chemistry. Predictions from the early years and comparison with recent experiments

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Abstract ISTCP Congress, July 11-17, 2019, Trømso, Norway

A variety of processes originating from the interaction of atomic or molecular N-electron states with strong and/or hypershort radiation pulses can be understood quantitatively only by first determining with good accuracy the solutions of the many-electron time-dependent Schrödinger equation (METDSE) that describe the corresponding physics. The METDSE is solvable nonperturbatively via the *state-specific expansion approach* (SSEA), introduced in the early 1990s [1]. SSEA solutions have been used, or can be used, for quantitative explanation and numerically reliable predictions of quantities that have been measured or are measurable in modern experiments that can track, with hypershort time resolution, the effects of electron dynamics in atoms and molecules. The calculations take into account in a transparent way the interplay between the phenomena and the electronic structures of the physically significant states in discrete and multichannel continuous spectra, including multiply- and inner-hole–excited resonance states.

Soon after the announcement in 2001 of the first generation of attosecond pulses in the laboratory, in a series of papers starting in 2002 [2,3], we proposed and demonstrated from first principles, via the implementation of the SSEA, that coherent excitation and decay of strongly correlated resonance (autoionizing, Auger) states constitute a fertile domain for the then nascent attosecond spectroscopy, where effects of state-superpositions, of electron correlations and of electron rearrangements can be resolved on attosecond scales.

The lecture will discuss briefly key elements of the SSEA, and will include a comparison of our predictions from 2007 [4] and 2010 [5] with quantitative attosecond-resolved measurements of novel phenomena, such as, 1) the time-dependent build-up of the profile of the He $2s2p\ {}^1P^o$ resonance state during photoionization [4,6], and, 2) the recognition that there is a *relative time delay* of the order of about 10 attoseconds in the photoejection of the ($2s, 2p$) electrons of Neon [3,5,7].

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VeloxChem: an efficient implementation of real and complex response functions at the level of Kohn–Sham density functional theory

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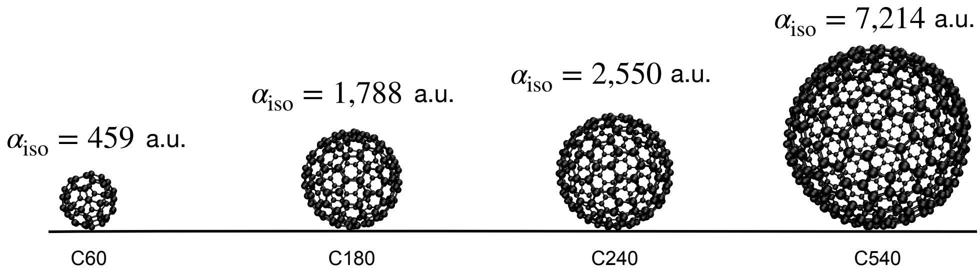
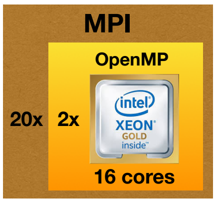
With the ease of Python library modules, VeloxChem offers a front end to quantum chemical calculations on contemporary high-performance computing (HPC) systems and aims at harnessing the future compute power within the EuroHPC initiative. At the heart of this software lies a module for the evaluation of electron-repulsion integrals (ERIs) using the Obara-Saika recurrence scheme, where a high degree of efficiency is achieved by employing architecture-independent vectorization via OpenMP SIMD pragmas in the auto-generated C++ source code. The software is topology aware and with a Python-controlled work and task flow, the idle time is minimised using an MPI/OpenMP partitioning of resources.

In the second software layer, we have implemented a highly accurate SCF start guess based on atomic densities and a first-level of iterations in a reduced version of the user-defined basis set, leading to a very smooth convergence in the subsequent standard DIIS scheme. This layer also includes vectorised and OpenMP/MPI parallelised modules for efficient generation of DFT grid points and weights as well as kernel integration.

In the third software layer, we present real and complex response functions as to address dispersive and absorptive molecular properties in spectroscopy. The kernel module in this layer is the iterative linear response equation solver that we have formulated and implemented for a combination of multiple optical frequencies and multiple perturbation operators. With efficient use of computer memory, we enable the simultaneous reference to, and solving of, in the order of 1,000 response equations for sizeable biochemical systems without spatial symmetry, and we can thereby determine electronic response spectra in arbitrary wavelength regions, including UV/vis and X-Ray, without resolving the sometimes embedded excited states in the spectrum. E.g. the electronic CD spectrum (involving the Cartesian sets of electric and magnetic perturbations) over a range of some 10 eV is obtained at a computational cost comparable to that of determining the transition energy of the lowest excited state, or optimising the electronic structure of the reference state.

Multi-frequency/gradient linear response equation solver





Fullerene	C60	C180	C240	C540
No. basis functions	840	2,520	3,360	7,560
No. iterations	14	13	12	14
Wall time, sec	**289**	**3,098**	**5,373**	**38,036**

Selectivity models for chemical synthesis

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Selectivity is an essential component in planning a synthetic route to a target compound. A low selectivity implies a low yield and tedious purification. At AstraZeneca, we try to support the route finding process by making mechanistically based predictive tools available to synthetic chemists with no modeling experience. The current presentation will focus on two types of selectivity:

- Enantioselectivity is the crucial property of asymmetric catalysts. Using our Q2MM methods to create reaction-specific transition state force fields [1], we have created a virtual screening tool that calculates the expected selectivity for a given substrate with a pre-defined library of chiral catalysts [2].
- Regioselectivity is the ability to predict the reaction site when multiple positions can be attacked. This is especially a difficult task in C-H functionalization reactions, which are at the core of the late stage functionalization strategy (LSF) . We are training machine learning models to predict sites of reactivity using computed descriptors [3]. With a sufficient number of reactions in the final tool, the chemists will be able to select the most well-suited reaction class for each desired C-H functionalization in complex scaffolds.

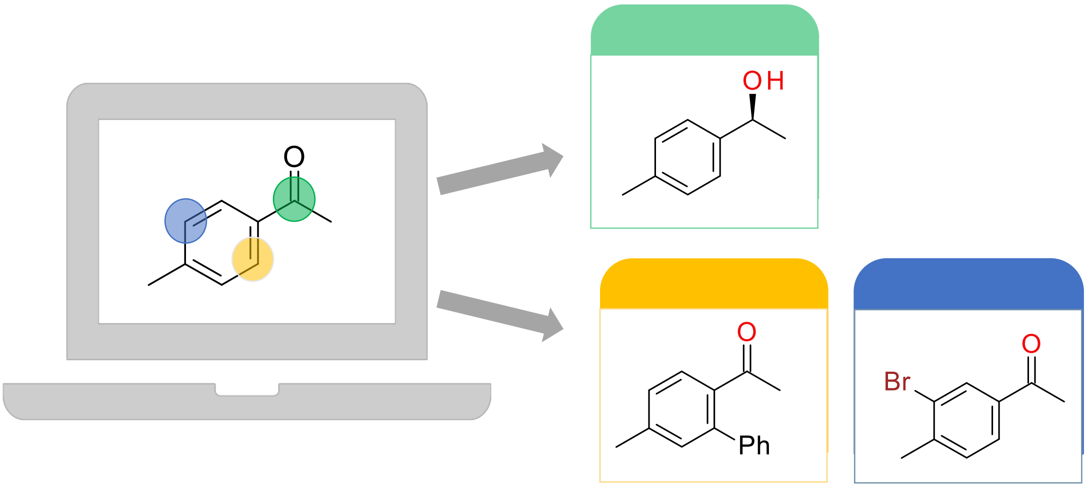

Figure 1: computational modelling of reaction selectivity.

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Quantum-chemical methods for biochemical systems

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Linear- and sublinear-scaling methods ranging from DFT, MP2 to RPA allow - in particular in combination with graphics processing units (GPUs) - for the description of biochemical systems at QM and QM/MM levels. Here, large QM spheres with typically 500-1000 atoms are necessary for reliable studies [1]. Linear-scaling methods are briefly outlined with special focus on our RPA (random-phase approximation) [2, 3] and beyond RPA [4] reformulations for describing electron-correlation effects using atomic orbitals and Cholesky-decomposed densities. Furthermore, we introduce a new resolution-of-the-identity (RI) scheme for MP2 and RPA which avoids entirely the huge errors in absolute energies of standard RI approaches. In contrast to standard RI that typically relies on error cancellations for relative energies, our RI scheme for MP2 and RPA is almost error free, while the cost is only slightly increased [5]. Applications of our linear-scaling quantum-chemical methods range from understanding the discrimination within the nucleotide addition reaction in RNA polymerase II [6], over the dynamical behavior of PYP (photoactive yellow protein) [7], to a new base-independent DNA repair mechanisms [8]. Finally, a widely applicable approach for localizing free energy changes is introduced [9] that allows for novel insights into molecular transformations.

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Properties of Molecular Electrolytes

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The physical properties of complex molecular electrolytes are essential for biological function and of great interest to industry. They have been particularly difficult to describe theoretically and computationally given the presence of dielectric heterogeneities and the large number of disparate length scales involved in determining their physical properties. The Debye length, the Bjerrum length, the ion size, the molecular structure, and the special charge distribution along the molecules with charged and neutral groups such as amphiphiles and proteins determine their structure and their response to external stimuli. Computational, numerical and theoretical approaches to describe electrolytes in bulk, solutions and at interface will be described and a conceptual understanding of how charge dictates nano-scale structure and function will be provided.

Nuclear Quantum Effects in Ion-Mediated Hydrogen-Bond Rearrangements

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A microscopic picture of hydrogen-bond structure and dynamics in ion hydration shells remains elusive. In this context small aqueous ionic clusters represent ideal systems to investigate the interplay and competition between ion–water and water–water interactions as well as the role played by nuclear quantum effects in hydrogen-bond rearrangements. Here, we perform quantum dynamics calculations on data-driven many-body potential energy surfaces to unravel specific ion effects in hydrogen-bond rearrangements in small $X^{-}(H_2O)_n$ complexes (X = F, Cl, Br, and I). Our results provide evidence for tunneling in hydrogen-bond rearrangements in both halide–dihydrate and halide–dihydrate complexes. Furthermore, a systematic analysis of hydrogen-bond rearrangements in the $X^{-}(H_2O)_2$ complexes at low temperature the provides fundamental insights into the competition between halide–water and water–water interactions depending on the properties of the halide ion. While the halide–water hydrogen-bond strength decreases as the size of the halide ion increases, the opposite trend is observed in the strength of the water–water hydrogen-bond, suggesting that nontrivial many-body effects may also be at play in the hydration shells of halide ions in solution, especially in frustrated systems (e.g., interfaces) where the water molecules can have dangling OH bonds.

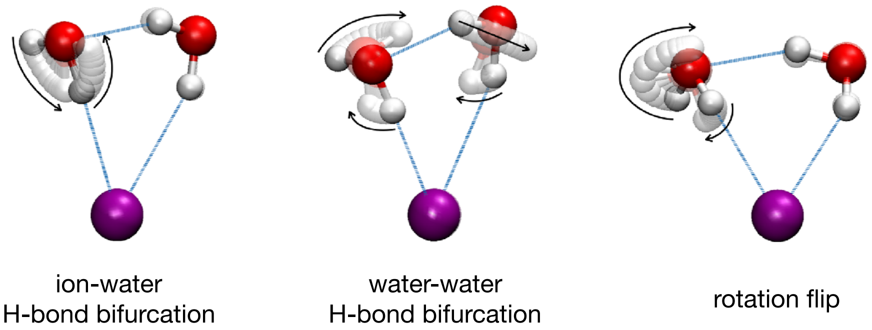

Figure 1: Tunneling pathways in the $X^{-}(H_2O)_2$ complexes.

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New Mechanisms and Concepts for Organic Reactivity and Enantioselectivity From Computations

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The development of new asymmetric catalytic methods is experimentally challenging. It is also difficult to compute: multiple non-covalent interactions and solvation effects influence structures and stabilities. As a result, computational analyses have often lagged behind empirical studies. I will describe the result of collaborative studies in which mechanistic understanding and quantitative predictions derived from computation have led to new and improved experimental designs.[1] In particular, we have explored the mechanism and selectivity of several transformations proceeding via ion-pairing.[2] Computational studies have been used to design new catalyst structures which have been experimentally validated,[3] leading to new methods to control the reactivity and selectivity of ionic reagents in solution.[4,5]

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Combined computational and spectroscopical analysis of tetravalent f-element complexes

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The rich chemistry of actinide complexes makes them an interesting object for scientific investigations. This resulting enthusiasm can be curbed by the difficulties that arise in the treatment of actinides, both *in vitro* and *in silico*. It is of course the partial filled f-shell and the similarity of the f and d orbital energies, that make especially the first half of the actinide row sow interesting, see e.g. [1]. Computationally as well as experimentally it is interesting and educating to compare lanthanide and actinide complexes.
We present here an analysis of the electron density of several salene and amidinate complexes of tetravalent actinides and lanthanides (See Figure 1) that have been synthesised in our laboratories.

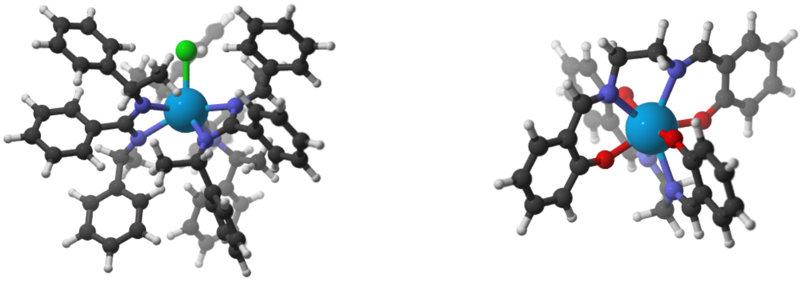

Figure 1: Structure of the amidinate complex [ThCl((S)-PEBA)$_3$] (left) and of the Schiff-base complex [Th(Salen)$_2$] (right).

The complex structures were optimised at DFT level and subjected to QTAIM analysis, we will also present density difference plots and plots of weak interactions (known as non-covalent interaction plots, NCI). We then proceeded to multi-reference calculations, some preliminary results will be shown.
We then discuss some features of the NMR spectra of these complexes. Finally we will present some features of the UV/VIS and TRLFS spectra of selected actinide complexes.
Our results should help to improve the understanding of actinide bonding. This will then allow us to predict the behaviour of actinides in the environment as well as in technical processes. This knowledge is of course important in amongst others, the context of nuclear waste disposal.

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Dynamic Correlation for CASSCF Reference with Adiabatic Connection Approaches: Open Shell Systems and Dispersion Interaction

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Correlation energy, despite being a small fraction of the total electronic energy, governs binding of atoms into molecules. Similarly, noncovalent molecular interactions are flawed if the correlation of electrons belonging to interacting subsystems is not accounted for. Many-electron methods aim at predicting correlation energy of the short- and long-range type. The two main approaches to electron-correlation involve either perturbation theory or are based on density functionals. They are deficient either in accuracy or computational efficiency and a generally applicable, computationally efficient approach remains a challenge.

Recently we have proposed a novel approach to describing electron correlation in multireference systems by adopting the adiabatic connection (AC) formalism [1]. The latter naturally links electron correlation with fluctuation of density at different points in space. Consequently, the final expression for the correlation energy employs linear response properties. In our formalism, we use extended random phase approximation (ERPA) to describe the latter.

The proposed AC-ERPA method yields excellent results for ground and excited states of molecules described with the CASSCF wavefunction [2,3]. The AC and its inexpensive approximation AC0 method compete or surpass in accuracy the perturbation (PT2 or NEVPT2) corrections. Unlike the latter methods, the AC approximations do not require construction of higher than two-particle reduced density matrices.

AC methods have been extended to arbitrary spin symmetry of the reference CASSCF sate and successfully applied to open-shell systems [4]. Application of the AC0 method to description of tetramethyleneethane (TME) diradical reveals that that AC0 rather closely reproduces the FCIQMC benchmark for singlet and triplet states. It has also led to elucidation of the interplay of dynamic and static correlation as a decisive factor for understanding the shape of the diradical's potential energy surfaces.

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On the Development of Accurate Gaussian Basis Sets for f-Block Elements - Initial Efforts for F12 Correlation Consistent Basis Sets for Uranium

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Over the last few years, the Peterson group has developed sequences of correlation consistent basis sets for the f-block elements La-Lu and Ac-Lr [1-3]. These were mostly all-electron sets based on either the Douglas-Kroll-Hess or eXact 2-component scalar relativistic Hamiltonians, but additional sets based on relativistic effective core potentials were also developed for Th-U. All of these basis sets, which included those for both valence and outer-core correlation, exhibited systematic convergence to both the Hartree-Fock and correlation energy complete basis set (CBS) limits, but exhibited relatively slow convergence, particularly for correlation of the outer-core. Based on our previous experience with explicitly correlated F12 methods [4], these should be very efficient at recovering correlation effects of electrons in the compact inner valence orbitals, e.g., the 5f of the actinides, as well as the important outer-core electrons, e.g., the 5s5p5d of actinides. Initial results for geometries and relative energies will be presented at the CCSD(T)-F12 level of theory using existing cc-pV*n*Z-PP basis sets for selected uranium-containing molecules. Preliminary design of new F12 basis sets for uranium will also be discussed.

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Computational modeling of H/H+ migration in porous and layered materials

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Spatial confinement has strong impact on the chemical properties of molecules. The layers of *h*-BN, MoS_2, and graphene are chemically very stable, if not inert, and the interlayer interactions impose pressure on the intercalated species. So, the chemistry in the interstitial space of a layered material is expected to be significantly different from the surface-adsorbed counterpart. Based on first-principles calculations combined with well-tempered metadynamics simulations, we report the chemical interactions and mobility of protons (H^+) and protium (H) in the interstitial space of these layered materials. We show that both H^+ as well as H can be transported between the layers of *h*-BN and MoS_2 with low free energy barriers, while they are immobilized in graphite, in accordance with experimental observations.

In the case of anhydrous proton conducting porous materials like COFs and MOFs, the conductivity of the proton is mediated by guest molecules like imidazole, triazole etc. that operate at relatively high temperature [1,2]. Another type of materials that serve, as proton conductors, are the so-called materials with intrinsic proton conductivity. In these materials there is no need from a guest molecule to facilitate the proton conductivity [3]. In the second part of the talk we will discuss an opportunity to use a functionalized with acidic groups porous aromatic polymers as a materials with intrinsic proton conductivity.

In the last part of the talk the dynamics of a H+ from acidic zeolite OH – groups in the zeolite frameworks, containing transition metal clusters will be discussed. On the basis of ab-initio MD simulations we will show that that reversed spillover of hydrogen is a spontaneous process and modifies the properties of the active cite (transition metal cluster).

Acknowledgements: PPetkov is thankful to the project No: КП-06-Д002/2.

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Toward Exact Quantum Chemistry by a Combination of Stochastic Wave Function Sampling and Deterministic Coupled-Cluster Computations

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One of the main goals of electronic structure theory is to precisely describe increasingly complex polyatomic systems. It is widely accepted that size extensive methods based on the coupled-cluster (CC) theory and their extensions to excited states via the equation-of-motion (EOM) formalism are excellent candidates for addressing this goal. Indeed, when applied to molecular properties and chemical reaction pathways, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, etc., rapidly converges to the limit of the exact, full configuration interaction (FCI), diagonalization of the Hamiltonian, allowing one to capture the relevant many-electron correlation effects in a conceptually straightforward manner through particle-hole excitations from a single Slater determinant. One of the key challenges has been how to incorporate higher–than–two-body components of the cluster operator, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes, while eliminating failures of the more practical perturbative approximations of the CCSD(T) type in multi-reference situations, such as chemical bond breaking. In this talk, we examine a radically new way of obtaining accurate energetics equivalent to high-level CC calculations, even when electronic quasi-degeneracies become significant, at the small fraction of the computational cost, while preserving the black-box character of single-reference computations. The key idea is a merger of the deterministic formalism, abbreviated as CC(P;Q) [1,2], with the stochastic CI [3,4] and CC [5] Quantum Monte Carlo (QMC) approaches [6]. We also demonstrate that one can take the merger of the stochastic and deterministic ideas to the ultimate level and use it to enable precise extrapolations of the exact, FCI, energetics based on the early stages of FCIQMC propagations [7]. The advantages of the new methodologies will be illustrated by molecular examples, where the goal is to recover the nearly exact, CCSDT and CCSDTQ, and exact, FCI, energetics in situations involving chemical bond dissociations and reaction pathways. Extensions of this work to excited electronic states by a combination of stochastic CIQMC and deterministic EOMCC computations [8] and converging FCI energetics in strongly correlated systems, such as those involved in modeling metal–insulator transitions [9], will be mentioned as well.

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Scalable polarizable molecular dynamics using Tinker-HP

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Tinker-HP [1] (http://tinker-hp.ip2ct.upmc.fr/) is a CPU based, double precision, massively parallel package dedicated to long polarizable molecular dynamics simulations and to polarizable QM/MM. Tinker-HP is an evolution of the popular Tinker package [2] (http://dasher.wustl.edu/tinker) that conserves it simplicity of use but brings new capabilities allowing performing very long molecular dynamics simulations on modern supercomputers that use thousands of cores. The Tinker-HP approach offers various strategies using domain decomposition techniques for periodic boundary conditions in the framework of the (N)log(N) Smooth Particle Mesh Ewald. Tinker-HP proposes a high-performance scalable computing environment for polarizable force fields giving access to large systems up to millions of atoms. I will present the performances and scalability of the software in the context of the AMOEBA force field. Various benchmarks and examples on biomolecular systems will be provided on several architectures. As the present implementation is clearly devoted to petascale applications, the applicability of such an approach to future exascale machines will be exposed and future directions of Tinker-HP discussed in the framework of our ERC SYG EMC2 project. New results towards large scale QM/MM hybrid simulation coupling polarizable force fields and Density Functional Theory (DFT) [3] will be presented.

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Time-Domain Modeling of Excited State Dynamics in Halide Perovskites

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Photo-induced processes play key roles in photovoltaic and photo-catalytic applications of halide perovskites, requiring understanding of the material's dynamical response to the photo-excitation on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques,[1] implemented within time-dependent density functional theory,[2-4] allow us to model such non-equilibrium response in the time domain and at the atomistic level. Considering realistic aspects of perovskite structure,[5] we demonstrate that strong interaction at the perovskite/TiO_2 interface facilitates ultrafast charge separation,[6] how dopants can be used to both decrease and increase charge recombination,[7-9] that grain boundaries constitute a major reason for charge losses,[9] that moderate humidity increases charge lifetime, while high humidity accelerates losses,[10] that hole trapping by iodine interstitial, surprisingly, extends carrier lifetime,[11] that collective nature of dipole motions inhibits nonradiative relaxation,[12] that organic cation orientation has a strong effect on inorganic ion diffusion and current-voltage hysteresis,[13] that surface passivation with Lewis base molecules decelerates nonradiative charge recombination by an order of magnitude,[14] that the experimentally observed dual (hot/cold) fluorescence originates from two types of perovskites substructures,[15] that doping with larger cations increases lattice stiffness and slows down nonradiative charge recombination,[16] why PbI_2 rich perovskites show better performance,[17] that halide composition can be used to control charge relaxation,[18] that oxidation states of halide defects strongly influence charge trapping and recombination,[19] and why perovskites exhibit unusual temperature dependence of electron and hole lifetimes.[20]

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Cavity-induced collective dissipation for cold chemistry

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Cavity-induced collective dissipation for cold chemistry

Strong light-matter interactions are playing an increasingly crucial role in the understanding and engineering of new states of matter with relevance to the fields of quantum optics, solid state physics and materials science. In this talk we discuss the opportunity to combine cavity quantum electrodynamics and cold chemistry, by utilizing an optical cavity to form ground-state molecules from ultracold atoms. We propose theoretically that collective effects in the dissipative dynamics can provide a robust alternative to current techniques, such as photoassociation or STIRAP-based techniques. We conclude with a perspective of possible applications of cavity-QED in cold chemistry and materials science.

Rotational Spectroscopy Meets Quantum Chemistry for Elucidating Astrochemical Challenges

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Cosmic evolution is the tale of progressive transition from simplicity to complexity. The newborn universe starts with the simplest atoms formed after the Big Bang and proceeds toward "astronomical complex organic molecules" (aCOMs). Understanding the chemical evolution of the universe is one of the main aims of Astrochemistry, with the starting point being the knowledge whether a molecule is present in the astronomical environment under consideration and, if so, its abundance. In this context, molecular spectroscopy plays the central role: because of the tremendous distances involved, there is no chance to do direct experiments on astrochemical processes, and detection via interaction of molecules with radiation is the only viable route of investigation. The astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence in the astronomical environment under consideration, with the overwhelming majority of gas-phase chemical species being discovered via their rotational signatures [1-3]. However, the interpretation of astronomical detections and the identification of molecules are not all straightforward.

Among the goals of astrochemistry, the detection of prebiotic aCOMs in astrophysical environments, and in particular in star forming regions, is fundamental in view of possibly understanding the origin of life. While, nowadays, the evidence for molecular complexity in the universe is undisputed, there is still much to be understood about what prebiotic molecules are present and how they are formed in the typically cold and (largely) collision free environment of the interstellar medium. By means of selected examples [4-7], it will be shown that: (*i*) state-of the-art computational approaches are required to derive structures, energies, spectroscopic properties, and thermochemical data for an accurate characterization of the prebiotic aCOMs under consideration and their potential precursors [3,8]; (*ii*) crucial challenges in astrochemistry can be successfully overcome by combining state-of-the-art computational spectroscopy approaches [9] with experiment in the field of rotational spectroscopy.

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Fundamental and approximate symmetries, parity violation and tunnelling in chiral and achiral molecules

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Symmetry and asymmetry are concepts, which are used in a wide range of contexts, from the fundamental sciences, mathematics, physics, chemistry and biology to the arts, music and architecture [1]. If asymmetries are small , one may still introduce the concept of approximate symmetries . Symmetries can be associated with constants of the motion. Particularly interesting approximate molecular symmetries are nuclear spin symmetry and parity, resulting in approximate constants of the motion. We shall start with an introductory outline of how symmetries can be applied to the understanding of the time scales in fundamental kinetic primary processes. We then briefly discuss our approach to derive molecular quantum dynamics from high resolution spectroscopy with some selected examples from our recent research including results on molecular tunnelling and tunnelling switching phenomena in free molecules and including excitation with coherent time dependent fields. Of particular interest is the control of symmetry by external fields. These lead to interesting nonclassical states recently introduced for molecular quantum switches in our work .We shall also report on current progress towards the observation of the theoretically predicted, new process of parity change with time in isolated chiral molecules, which connects the principles of high energy physics with molecular chemical kinetics and potentially the evolution of biomolecular homochirality. We shall present our most recent analyses of high resolution infrared, THz and GHz spectra of relevant chiral and achiral molecules as available at the time of the meeting and relevant in this context. For background reading and some recent results see [1-12], and www.ir.ETHz.CH (lecture Tromsoe July 2019)

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Shielding ultracold molecules against losses in collisions

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Ultracold dipolar molecules are excellent candidates for engineering quantum applications and cold, controlled chemistry [1]. Therefore a lot of effort is devoted nowadays to produce ground state ultracold molecules in high densities as well as to understand their properties [2]. One of a main goal is to create a quantum degenerate gas of dipolar molecules such as a Bose-Einstein condensate or a degenerate Fermi gas. This is for now a major missing step for ultracold molecules.

Unfortunately, when the molecules start to collide, whether they are chemically reactive or not, a lot of molecules are lost in the process. Hoping for a long-lived quantum degenerate gas is then compromised unless to shield the molecules from collisional losses. This can be achieved by using a static electric field [3] but also by using microwaves [4,5,6]. By applying a circularly polarized and slightly blue-detuned microwave field with respect to the first excited rotational state of a dipolar molecule, one can [6]:

(i) bring the ratio good to bad collisions $\gamma = \beta^{el}/\beta^{qu}$ (elastic over quenching rate coefficient) to high values such that evaporative cooling techniques can be successful,

(ii) suppress the imaginary part of the scattering length and shield the molecules against losses,

(iii) tune the real part of the scattering length to small or large values, positive or negative and control the interaction strength of an ultracold molecular gas.

This theoretical proposal might be a requirement for successful evaporative cooling of molecules and for reaching quantum degeneracy. The ability to control the molecular scattering length is also important for many-body physics applications, as it is already for ultracold atoms.

I acknowledge the financial support of the FEW2MANY-SHIELD project (#ANR-17-CE30-0015) from Agence Nationale de la Recherche in France.

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Understanding enzymatic reactions

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We know that we can establish catalytic mechanisms of enzymatic reactions and, in doing so, explain the findings of experimentalists, but can we actually predict them? This talk is concerned with the computational needs that we come across to figure out results within computational enzymology. Calculations devised to study protein interactions and circumvent problems in some relevant systems will be reported as well as recent developments in the establishment of some catalytic mechanisms. We have resorted to QM/MM [1,2] as well as other calculations [3,4], in order to analyse the energetics of processes related to the systems under study and evaluate their feasibility according to the available experimental data.

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Quantum Chemical Exploration of Catalytic Reaction Networks

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A variety of different approaches have been proposed for the automated exploration of complex reaction networks of a variety of chemical processes in the last decade.[1] In such an endeavor, we have followed a specific path which combines massively automated exploration[2] based on first-principles heuristics with interactive steering[3] through real-time quantum mechanics[4]. As results of individual calculations can no longer be carefully inspected owing to the huge amount of data produced, we improved on standard algorithms in order to make orbital optimizations more robust[5] and fast[6] and to push the stability of transition-state optimization[7]. We equipped all steps with error estimation procedures[8] that together with seamless uncertainty quantification[9] allow for kinetic modelling and mechanism deduction from noisy reaction networks[10]. A specific design feature of our approach has been the drive to provide algorithms that are agnostic w.r.t. the type of molecules considered and that can be extended when needed. In my talk, I will describe this integrated approach that led to the SCINE project (www.scine.ethz.ch).

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Lecture: Lec-157

Spatial and temporal localization of the vibronic and photoelectron wave packets in LiH photoexcited by intense few cycle IR pulses

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Few-cycle ultrashort IR pulses allow excitation of coherently coupled electronic states towards steering nuclear motions in molecules. The progress of the non stationary vibronic density towards the products can be monitored using a second pulse, by transient absorption spectroscopy or photoionization. The Hamiltonian includes the pump and probe pulses which provides a quantum mechanical description of both multiphoton excitation and ionization. For pumping, we use an IR pulse with a controlled phase between its envelope and carrier wave. We report on the interplay between photoexcitation and photoionization in shaping the ensuing coupled electronic-nuclear dynamics in both the neutral excited electronic states and the cationic states of the diatomic molecule LiH. The dynamics is described by solving the time-dependent Schrodinger equation at nuclear grid points using the partitioning technique with a subspace of ten coupled bound states and a subspace of discretized continuous states for the photoionization continua. We show that the coherent dynamics in the neutral subspace is strongly affected by the amplitude exchanges with the ionization continua during the pulse, as well as by the onset of nuclear motion which drives non adiabatic interactions in the Franck-Condon region and on the way to the reaction products. Our methodology provides a visualization in space and in time of the entanglement between vibronic wave packet in the neutral states and the wave packet of the outgoing photoelectron.

All-electron relativistic four-component Dirac–Kohn–Sham theory for solids using Gaussian-type functions

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First-principle predictions of electronic structure and properties of solid-state materials containing heavy elements pose numerous challenges to computational methods, as the variational treatment of relativistic effects is in many cases required and multiple wavefunction components coupled by the spin–orbit interaction increase the complexity of the formalism and the computational cost. Here, we present a four-component Dirac–Kohn–Sham theory for obtaining relativistic band structures of spin–orbit-coupled solids. The method was recently developed in our group [1,2], and uses restricted kinetically balanced Gaussian-type orbitals (GTOs) to compactly express all operators in real space. The atom-centered nature of GTOs allows for explicit handling of one-, two-, and three-dimensional periodic systems while avoiding the need to introduce vacuum layers. We provide a detailed description of how key components of such a method are altered in the four-component regime, and show the necessary steps that need to be overcome when employing GTOs on periodic systems. Finally, we demonstrate the validity of the method on 3-dimensional silver halide (AgX) crystals with strong scalar-relativistic effects, and 2-dimensional honeycomb structures (silicene and germanene) exhibiting the quantum spin Hall effect due to a strong spin–orbit coupling.

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Interfacial choline-aromatic cation-π interactions can contribute as much to peripheral protein affinity for membranes as aromatics inserted below the phosphates

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Peripheral membrane proteins populate both soluble and membrane-bound forms. Unlike transmembrane proteins, peripheral binders rely on membrane binding interfaces that are restricted to a small part of their exposed surface and the ability to engage in strong selective interactions with membrane lipids at various depths in the interface, both below and above the lipid phosphates, is an advantage. While aromatic amino acids preferentially partition into membrane interfaces driven by their hydrophobicity, enthalpically favorable interactions with the lipid headgroups are likely to further stabilize high interfacial positions. Yet the role of aromatics in the binding of peripheral proteins to membrane has historically been restricted to that of deep hydrophobic anchors.

Using molecular simulations in combination with experimental affinity data, we could show that tyrosine residues of a bacterial phospholipase interact with the headgroups of phosphatidylcholine-containing lipids via cation−π interactions (Figure 1) [1]. We then evaluated the ability of molecular mechanics force fields to represent the structure and energetics of aromatics-choline cation−π interactions, and subsequently proposed modifications of the CHARMM force field [2,3]. More recently we used Free Energy Perturbation to calculate the energetic cost of alanine substitution for 11 interfacial aromatic amino acids from 3 peripheral proteins [4]. We showed that involvement in cation-π interactions with the headgroups (i) increases the $\Delta\Delta G_{transfer}$ as compared to insertion at the same depth without cation-π stabilization and (ii) can contribute at least as much as deeper insertion below the phosphates, highlighting the multiple roles of aromatics in peripheral membrane protein affinity.

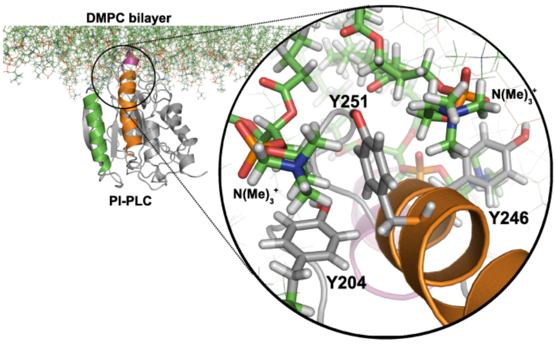

Figure 1: Cation−π interactions between a bacterial phospholipase and a lipid choline [1]

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Nonadiabatic quantum transition-state theory

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We propose a new quantum transition-state theory (GR-QTST) for calculating Fermi's golden-rule rates in complex multidimensional systems [1]. This method is able to account for the nuclear quantum effects of delocalization, zero-point energy, and tunnelling in an electron-transfer reaction. It is related to instanton theory [2] but can be computed by path-integral sampling and is thus applicable to treat molecular reactions in solution. A constraint functional based on energy conservation is introduced which ensures that the dominant paths contributing to the reaction rate are sampled. We prove that the theory gives exact results for a system of crossed linear potentials and show numerically that it is also accurate for anharmonic systems. It is also seen to perform well for multidimensional spin-boson models, where it even gives good predictions for rates in the Marcus inverted regime.

We demonstrate that for systems exhibiting two or more transition states, rates computed using Wolynes theory [3] can be overestimated by orders of magnitude, whereas the GR-QTST predictions are numerically accurate. This is the case both at low temperature, where nuclear tunnelling makes a considerable contribution, and also in the classical limit, where only GR-QTST rigorously tends to the correct result. Analysis shows that the saddle-point approximation employed by Wolynes theory is not valid in this case and that the method is unphysically dominated by paths located far from the correct transition states. The energy constraint employed by GR-QTST resolves this problem. For a system with strong anharmonicity, where the semiclassical approximations of instanton theory are not valid, the GR-QTST method, which samples configurations around the instanton pathway, is seen to give accurate results. These promising results indicate that the GR-QTST method could be an efficient and accurate approach for simulating electron-transfer reactions in complex molecular systems.

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Lecture: Lec-161

Stimulated X-Ray Emission Spectroscopy for Chemical Analysis

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X-ray free-electron lasers (XFEL) deliver X-ray pulses of fs duration, at unprecedented intensities that open avenues for studying nonlinear optical effects and stimulated X-ray emission and scattering. An intriguing future perspective is the development of coherent attosecond nonlinear pump-probe techniques, to study charge and energy transport in chemical reactions and photocatalysis. Stimulated X-ray emission and stimulated X-ray scattering are the fundamental building blocks of these nonlinear spectroscopic techniques. Here we present results on amplified spontaneous K-α spectroscopy of Mn compounds in solution [1]. We show amplification of the K-α emission at 5.9 keV photon energy in $MnCl_2$ 5-molar solution by over 4 orders of magnitude up to a saturated signal, containing 10^6 detected photons in a single shot. The spectrum of the emission is studied as a function of the amplification and shows stark differences from the spontaneous K-α spectrum: For low amplification we could demonstrate gain narrowing with an emission width below the natural life time width of the 1s core hole. In the exponential gain region, the stronger K-α_1 component outcompetes amplification of the weaker K-α_2 line manifold. Within the K-α_1 spectral manifold we observe, that only a few of the underlying multiplet lines contribute to the spectrum. At high amplification levels, entering the strong-field limit, the lines get broader and show a shift towards the K-α_2 line at lower photon energies. All these measured features are well produced by our numerical simulation, based on the self-consistent solution of the Liouville – von Neumann equations for the ionic density matrix and Maxwell's equations in paraxial approximation. Results of $Mn(II)Cl_2$ are compared to $NaMn(VII)O_4$ emission spectra. These compounds contain Mn in different oxidation states, and the K-$\alpha_{1,2}$ emission energies are different by few eV. This shift in emission energy between different chemical compounds is termed chemical shift and is the essence of X-ray emission spectroscopy. Importantly, this energy shift in the emission peaks is clearly present in the stimulated emission spectra. Despite the stark differences to the spontaneous X-ray spectra, stimulated X-ray emission spectroscopy thus prevails the chemical sensitivity and opens the door to more advanced nonlinear X-ray spectroscopic techniques.

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Anharmonic Nuclear Quantum Effects and their Interplay with the Electronic Structure of Weakly Bonded Systems

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In this talk, I will discuss our recent efforts to include quantum nuclear effects in first-principles simulations of various high-dimensional systems containing weakly bonded organic components.

The quantum nature of the nuclei can often impact the atomic structure, nuclear dynamics, and the electronic structure of a given system at finite temperature. From a theoretical point of view, this requires simulations that treat electrons and nuclei as quantum particles, and that are also able to describe the coupling between them. Nuclear motion is most easily captured in the harmonic approximation, and improvements can be achieved by further perturbative expansions. However, in flexible organic systems, the anharmonic perturbation is typically large, such that the full anharmonic nature of the nuclear interactions has to be accounted for. In that respect, methods based on the path integral formulation of quantum mechanics arise as a good choice to treat anharmonic nuclear quantum effects in these systems.

I will present methodology to accelerate path-integral molecular dynamics of weakly bonded interfaces and to improve approximations to nuclear quantum dynamics [1,2] in a manner that allows their use with on-the-fly energy and force evaluations from first-principles methods [3]. We find important changes in the atomic structure, vibrational spectra, and reaction rate constants in the deep tunnelling regime for a wide class of systems comprising isolated molecules, organic-inorganic interfaces and molecular crystals [4-6]. In particular, we show that in weakly bonded interfaces anharmonic nuclear fluctuations can considerably change the electronic density of states and lead to isotope effects in the work-function of functionalized metallic surfaces.

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Molecular assemblies are often described using classical concepts and simulated using Newtonian dynamics or Classical Monte Carlo methods. At low temperatures, this classical description fails to capture the nature of the dynamics of molecules, and a quantum description is required in order to explain and predict the outcome of experiments. In this context, the Feynman path integral formulation of quantum mechanics is a very powerful tool that is amenable to large-scale simulations [1]. We will show how path integral simulations can be used to predict the properties of molecular rotors trapped in superfluid helium and hydrogen clusters [2]. We will show that microscopic Andronikashvili experiments can be viewed as a measurement of superfluidity in a quantum mechanical frame of reference. We will also show that path integral ground state simulations can be used to predict the Raman spectra of parahydrogen clusters [3] and solids. We will present ongoing work on the simulation of molecular rotors confined in endohedral fullerene materials such as H2O@C60 and HF@C60 [4]. The questions we will address include symmetry breaking, spin conversion, the nature of dipole correlations and dielectric response, and entanglement measures [5-7] in assemblies such as peapods (Fig. 1) and two-dimensional solids.

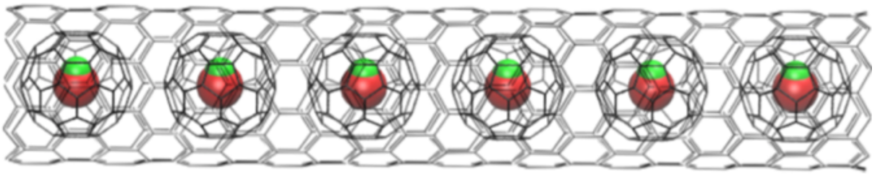

Fig. 1 Cartoon representation of an endofullerene peapod.

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Ab Initio Finite Temperature Auxiliary Field Quantum Monte Carlo for Solids

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Predicting the finite temperature properties of molecules, and especially, solids is critical for understanding many chemical and physical phenomena. Nevertheless, developing accurate, yet efficient methodologies for finite temperature applications remains an outstanding challenge. In this work, we present an Auxiliary Field Quantum Monte Carlo method with an $O(N^3)$ scaling for studying the finite temperature electronic structure of any system that can described by an *ab initio* Hamiltonian.[1] The algorithm marries the *ab initio* phaseless auxiliary field quantum Monte Carlo algorithm known to produce high accuracy ground state energies of molecules and solids with its finite temperature variant, long used by condensed matter physicists for studying model Hamiltonian phase diagrams, to yield a phaseless, *ab initio* finite temperature method. We demonstrate the accuracy of this approach for benchmark molecules, including the carbon dimer, and solids, including hydrogen chains and networks, and compare it to more popular mean field treatments of real materials. Our method serves as a new, robust tool for studying low, but finite temperature phase transitions in models and solids, ultracold chemistry, and warm dense matter.

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Molecules driven by light: Electron and nuclear dynamics

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Modern laser technology and ultrafast spectroscopies have pushed the timescales for detecting and manipulating dynamical processes in molecules from the picosecond over femtosecond domains (1 fs = 10^{-15} s), to the so-called attosecond regime (1 as = 10^{-18} s). This way, real-time dynamics of electrons and nuclei after their photoexcitation can be probed and manipulated. On the theory side, powerful quantum dynamical tools have been developed to rationalize experiments on photon-driven molecular species. In the talk, light-induced processes in molecular systems, ranging from "photophysics" and "photochemistry" – will be studied with the help of modern quantum chemistry and molecular quantum dynamics.

In a first, part laser-driven ultrafast electron dynamics will be followed with the help of wavefunction-based ab initio methods such as time-dependent configuration interaction (TD-CI) and the multi-configurational time-dependent Hartree-Fock (MCTDHF) method. Specific examples will be given for state-to-state transitions, creation of electronic wavepackets, and non-linear molecular response (High Harmonic Generation) and its control.

In a second part the vibronic spectroscopy of molecular systems will be considered. For species such as diamondoids the vibronic finestructure in electronic absorption, emission and photoelectron spectra is determined within a time-dependent correlation function approach. This approach has been suggested several decades ago by Heller and coworkers, and is now an efficient method for spectroscopy in complex molecular systems.

Finally, a step to photochemistry is made by considering photoswitching of molecules in an environment. Here, non-adiabatic molecular dynamics with surface hopping allow for detailed insight into the mechanism of photoinduced *trans*-to-*cis* isomerization of azobenzene molecules near surfaces.

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Ab initio Free Energy Calculations with Chemical Accuracy for Molecule - Surface Interactions

Solving problems in heterogeneous catalysis (hydrocarbon synthesis by zeolites) and gas separation (CO_2 capture and storage by MOFs - metal-organic frameworks) requires the reliable prediction of rate and equilibrium constants. With this aim in mind we have developed and applied methodology for the quantum mechanical *ab initio* prediction of *free energies* for large periodic systems (order of 1000 atoms) with chemical accuracy (4.2 kJ/mol). We have implemented a hybrid high level – low level approach combining accurate wave-function methods for the reaction site (“MP2”) with less accurate, but computationally more efficient density functional theory (DFT) calculations on the full periodic system. This approach is used for structure optimizations, whereas chemical accuracy for the energies is achieved after adding Coupled Cluster corrections with basis set extrapolation. We use molecular statistics (vibrational partition function) for efficient sampling of the potential energy surface. Chemical accuracy is reached with *anharmonic* vibrational frequencies. Calculation of the latter becomes possible by solving one-dimensional Schrödinger equations for each degree of freedom separately.

These methods yield free energies for the interaction of molecules with individual interaction sites. For predicting selectivities for gas separation, e.g. CH_4/CO_2 separation in MOFs, we use Grand Canonical Monte-Carlo simulations on a lattice of these sites. The Hamiltonian is defined by the free energies of adsorption on these sites and the lateral interaction energies of the molecules in the adsorbate layer.

The Year of the Periodic Table – Going Superheavy

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In the last decade we have seen the production of new elements for the Periodic Table up to nuclear charge 118. How far can we go? Where does the Periodic Table end and can we place the elements correctly into the Periodic Table as for example suggested by Pekka Pyykkö?[1] What chemistry can we do with such exotic elements?[2] What is the chemical and physical behavior of these exotic elements, and do we have to go beyond standard relativistic quantum mechanics to understand them? Recent developments in relativistic quantum theory have made it possible to obtain accurate electronic properties for the trans-actinide elements with the aim to predict their chemical and physical behavior.[3] We are now able, albeit with some computational effort and sophisticated algorithms, to correctly predict the aggregate state of these elements.[4] First-principles relativistic quantum simulations show that Cn is a liquid at standard conditions with a narrow temperature range to the gas phase,[5] behaving more like a rare gas, whilst Og shows a rather unusual Fermi-gas like behavior [6] being more reactive than the lighter rare gas elements and a semi-conducting solid at ambient conditions.[7,8]

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Quantum Chemistry for Strong Correlation

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Schrodinger's equation has been known for more than 90 years, yet many pressing questions in electronic structure theory remain unanswered. Quantum Chemistry is a successful field because for weakly correlated problems, we can get accurate answers at reasonably low polynomial computational cost instead of the combinatorial expense of brute force approaches. Despite many advances, however, the so-called strong correlation problem, where the chemist's molecular orbital picture breaks down, remains quite open, particularly for large molecules and solids. This lecture will address challenges and progress on the treatment of strong correlation, and its connection with quantum symmetries and degeneracy. Methods recently developed in our research group for strong correlation will be discussed.

Relativistic equation of motion coupled cluster based on four-compoment Hamiltonians

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Methods based on the coupled cluster ansatz and employing four-component Hamiltonians are particularly appealing in treating the electronic structure of molecules containing heavy centers, due to their efficient treatment of electron correlation and spin-orbit coupling (SOC) [1] on the same footing, up to and including the superheavy elements, as well as to serve as benchmark to more approximate relativistic Hamiltonians, notably those where SOC is treated more approximately (see for instance [2] and references therein). In this contribution we discuss our recent implementation [3] in the Dirac program [4] of the equation of motion coupled cluster method for excitation energies (EOM-EE-CCSD), single electron attachment (EOM-EA-CCSD) and single electron detachment (EOM-IP-CCSD). We showcase the method by addressing the determination of the low-lying states of oxide radicals of group 17 elements (XO, X = Cl, Br, I, At, Ts), the excited and ionized states of the PuO_2 molecule in the gas phase [5], as well as the ionization energies of halide ions in water droplets [6]. In the latter case, we use the frozen density embedding approach to combine EOM-IP-CCSD (for the halogens) and the SAOP model potential (for the water molecules) to determine the ionization energies for the complete halide-droplet system, while sampling different nuclear configurations with snapshots obtained from classical molecular dynamics simulations with polarizable force fields [7].

This work has been supported by the French national agency for research, contract ANR-11-LABX-0005 chemical and physical properties of the atmosphere (CaPPA).

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Polynomial scaling multireference methods

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All methods that are used to describe static correlation in multireference quantum chemistry scale exponentially with the size of the active space. This means that one has to be extremely stingy in choosing the active space. This, in turn, implies that one cannot do a black box calculation by say including all orbitals in the valence space for a large system. I will demonstrate that this limitation can be lifted if one uses variational Monte Carlo that is both accurate for strong correlation and also scales polynomially with the size of the active space.

Another difficulty with active space methods is that one cannot calculate dynamical correlation by using multireference perturbation theory or multireference configuration interaction if the active space is large. I will show that this limitation can also be lifted by using stochastic methods that do not require any RDMs in the active space.

Density matrix renormalization group:
time-dependent formalism, light-emitting, carrier transport, and singlet fission

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Electron correlation and electron-phonon coupling are the competing factors in organic/polymeric functional materials. DMRG has been proposed by White to treat correlated system which has been successfully extended to quantum chemistry, for example for studying the low-lying excited state orderings problem in conjugated polymers [1]. We present here some of our recent progresses on developing the DMRG time-dependent formalism as applied to the optical spectra for molecular aggregates[2], carrier transport for organic semiconductors [3], and singlet fission phenomena in donor-acceptor conjugated polymers [4]. An inner space perturbation algorithm is also introduced to replace the expensive matrix diagonalization procedures [5].

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Polarizable embedding for biological systems: Modeling photoactive proteins with the Effective Fragment Potential method

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Accurate description of solute-solvent interactions is a key for understanding photochemical processes in biological systems. The effective fragment potential (EFP) is a polarizable model providing rigorous description of non-covalent interactions from first principles. When coupled to a QM region, hybrid QM/EFP methods belong to polarizable embedding schemes. Recently, we extended the EFP method to modeling flexible macromolecules and polymers, which allowed us to analyse importance of polarization for biological processes. We apply the new flexible EFP methodology to model excitonic interactions in the Fenna-Matthews-Olson photosynthetic protein. Specifically, we decompose effects of polarization, electrostatics, and short-range terms on electronic properties of pigments and demonstrate importance of a balanced description of solute-solvent interactions for predictive modeling of absorption and circular dichroism spectra of this protein.

Synthetic chiral light for extremely efficient laser-controlled chiral discrimination

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Distinguishing left- and right-handed molecular enantiomers is challenging, especially on ultrafast time scale. Traditionally one uses a chiral reagent, an object of known handedness, to determine the unknown handedness of a chiral molecule. In optics, one uses the spatial helix formed by circularly polarized light as a “chiral photonic reagent”. However, in optical domain the pitch of this helix – the light wavelength – does not match the size of the molecule, leading to very small chiral signals. In dipole approximation, which neglects the size of the molecule with respect to light wavelength, circularly polarized light is not chiral. Indeed, the Lissajous figure drawn by the tip of the electric field vector is confined to a plane: the dipole approximation turns chiral helix of light into a circle. Since the dominant optical response arises in the dipole approximation, it is destined to be the same in opposite molecular enantiomers.

We will introduce a new concept of synthetic chiral light [1], which is chiral already in the dipole approximation. Compared to the inefficient chiral reagent – the light helix in space, here the helix is in time. In synthetic chiral light the electric field vector draws a three dimensional chiral Lissajous figure, at every point in space. The key point is that this chiral structure will appear already in the dipole approximation. We will show how this chiral photonic reagent can be tuned to “react” with the desired enantiomer of a chiral molecule and not with its mirror twin, achieving the ultimate limit in efficiency of chiral discrimination. It applies both to light absorption and emission measurements.

We demonstrate our approach using high harmonic emission from propylene oxide. High harmonic generation (HHG) records the electronic response of matter to light with sub-femtosecond temporal resolution. Chiral HHG (cHHG) has been recently stablished as a powerful technique for chiral recognition, chiral discrimination and for ultrafast imaging of molecular chirality [2-7]. So far, experimental realizations of cHHG required the interplay between electric and magnetic interactions to drive enantio-sensitive response in chiral media, yielding moderate values of chiral discrimination, ranging from 2% up to 13% [2,6,7]. Ref. [8] suggests a new scheme exclusively based on electric dipole approximation outperforming by far other cHHG methods in the ability to detect chiral matter, but not yet in obtaining enantio-sensitive signal in intensity. Here we show that using synthetic chiral light we can achieve 200% chiral dichroism in high harmonic intensity generated from left and right propylene oxide molecules [1]. The simplicity of generating synthetic chiral light in a laboratory opens a broad field of shaping and controlling chiral matter with light on ultrafast time scale.

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From molecular properties to intermolecular interaction potentials

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Calculations of spectra of clusters, scattering cross-sections, properties of condensed phases and of biomolecular systems, as well as *in silico* material design have become mainstream methods in science and engineering and are expected to become even more important as computers pass the exaflop performance threshold. All such calculations require force fields, i.e., potential energy surfaces (PESs) which determine nuclear motions. We are now entering the era when physics-based PESs fitted to *ab initio* quantum mechanical calculations for dimers and trimers are becoming the potentials of choice in all these fields. Among *ab initio* methods, symmetry-adapted perturbation theory (SAPT) [1] is particularly well suited for such calculations due to its seamless connection to asymptotic interaction energies. Recently, generation of *ab initio* derived PESs became as simple as running standard electronic structure programs thanks to the automation of this process in the autoPES package [2].

An important part of the autoPES methodology is the use of asymptotic expansions of interaction energies derived from first principles. First, the molecular properties of monomers: multipole moments and static and dynamic polarizabilities are computed *ab initio*. The properties defined relative to the center of mass (COM) of each monomer are then expressed in terms of properties distributed among the atoms. This is necessary since the COM-based expansion (semi)converges only for very large separations R while the distributed expansion accurately reproduces the total SAPT interaction energies down to distances of about 1.5 times the radial van der Waals minimum separation. The use of the asymptotic expansion has several advantages: (a) one avoids expensive *ab initio* calculations in a large sector of the dimer configurations space; (b) the resulting PES is correct at all R; (c) a physical interpretation of the components of interaction energy is directly related to monomer properties and, therefore, also to experimental observables; (d) the same methodology can be applied to develop empirical force fields, i.e., such force fields would use *ab initio* asymptotics and fit only the repulsive components.

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New Meta-GGA "Workhorses" in Transition Metal Chemistry and SAPT

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The recently developed DFT meta-GGAs and their hybrids, such as SCAN, SCAN0, MVS, ωB97M-V, and our own LC-PBETPSS-D3, promise improvement over the well-established GGAs and hybrid GGAs developed some 10-20 years ago. Are these promises fulfilled? Most of the tests thus far have involved main-group chemistry (and from the first two periods). This work examines performance of these new methods in transition-metal chemistry and catalysis. The results are rationalized in terms of fractional charge/fractional spin errors. The issue of suitability of these new meta-GGAs in symmetry-adapted perturbation theory is also explored.

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Molecular modelling of hybrid-ion batteries

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Batteries have been a constant target of research and improvement but the competition in this field has never been as strong as nowadays. All sorts of devices rely on them starting from pacemakers and hearing aids through mobile electronic devices and electric cars to stations for storage and redistribution of energy obtained from renewable sources or excess energy from power plants. Therefore, any effort to enhance their performance is welcome.

There exist numerous types of batteries but those that have undergone the fastest progress in the past decades are the lithium-ion batteries. However, their demand is high, their price remains steep and the deposits of lithium are depleting. An attractive alternative pricewise are the sodium-ion batteries but they are less efficient for mobile applications. Therefore, hybrid-ion batteries could be a solution but it requires extensive research and design of all components: electrodes and electrolyte solutions.

The traditional electrode materials are of inorganic origin. Their replacement with organic ones will reduce the cost and the weight, will be flexible and, hopefully, will improve the performance. In the present, based on doped or functionalised carbonaceous materials are modelled by means of first principles methods and the type of interaction with some light metal ions is discussed. The non-aqueous solvents should provide the efficient mobility of the charge carriers. The electrolyte-solvent interplay is discussed in terms of coordination number of the ions, of the free energy of their solvation/desolvation, and of the competition between the solvated ions. The cations considered are Li^+, Na^+, and Mg^{2+} (neutralized by PF_6^-) and the solvent is ethylene carbonate.

The outcomes can serve as guidelines for enhancement of the performance of hybrid-ion batteries.

Acknowledgments: The research was supported by projects D09/13/2016, and the National Research Program E+, grant D01-214/28.11.2018. The Erasmus+ internship program and the mentorship of Prof. Patrik Johansson's group at Chalmers University of Technology is acknowledged.

Explicitly correlated F12 theory on modern electronic structure calculations

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Since the seminal work of Hylleraas,[1,2] explicitly correlated approaches have successfully ameliorated the slow basis set convergence of the correlation energy in molecular electronic structure calculations. We shall look back on the development of the F12 theory[3−5] focusing on our contribution to the field including the rational generator approach[6] exploiting the s-/p-wave cusp conditions in conjunction with the Slater correlation factor.[7] We will also present F12 calculations of large molecules such as organic photovoltaics materials using a hybrid MPI/OpenMP implementation for massively parallel computations.[8,9]

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The ExoMol project: molecular line lists for the opacity of exoplanets and other hot atmospheres

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The ExoMol project aims to provide comprehensive line lists for models of hot astronomical bodies which contain molecules [1]. These line lists can be huge: in excess of 10 billion lines for molecules such as methane or CH_3Cl. Studies show that as the temperature increases treating the very large number of weak lines is essential to model opacities correctly [2].
Line lists are computed using variational nuclear motion programs starting from *ab initio* potential energy and dipole moment surfaces. *Ab initio* dipoles can be computed with an accuracy than means the uncertainty in the resulting intensities is competitive with the best experiment [3]. However, even the best *ab initio* potentials give transition frequencies which are far from true spectroscopic accuracy. This particularly true for species containing transition metal atoms [4], some of whom, such as TiO, are known to be important in stellar atmospheres and are thought to control thermal inversion in some classes of exoplanets. As a result extensive use is made of experimental data to improve potential energy surfaces and other aspects of the calculation.
The calculated line lists for over 50 molecules are available as part of the ExoMol database (www.exomol.com) [5]. For each molecule/isotopologue of interest the database provides energy levels (and hence transition frequencies) and Einstein A coefficients, along with other key properties including lifetimes of individual states, temperature-dependent cooling functions, Landé g-factors, partition functions, cross sections, k-coefficients and transition dipoles with phase relations. These data are widely used not only for astrophysics but also terrestrial applications ranging from combustion modelling to molecular steering.

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Principal Domains in Local Correlation Theory

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The computational efficiency of local correlation methods is strongly dependent on the size of the domain of functions used to expand local correlating orbitals such as orbital specific or pair natural orbitals. Here we define a principal domain of order m as the subset of m one-particle functions that provides the best support for a given n-electron wavefunction. Our chosen metric is the maximal overlap criteria, which was used by Löwdin to define natural orbitals. We present an efficient linear scaling greedy algorithm for obtaining principal domains of projected atomic orbitals and demonstrate its utility in the context of pair natural orbital local correlation theory.

Lecture: Lec-180

Towards Exact Molecular Dynamics Simulations with Quantum Chemistry and Machine Learning

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I will discuss an efficient symmetric gradient-domain machine learning (sGDML) approach for constructing next-generation CCSD(T)-quality interatomic force fields for molecules. The sGDML implementation is able to reproduce global potential-energy surfaces of intermediate-sized molecules with an accuracy of 0.1 kcal/mol using only few hundred molecular conformations for training. We demonstrate this accuracy for *ab initio* molecular dynamics (AIMD) trajectories of molecules, including toluene, naphthalene, ethanol, uracil, and aspirin. The GDML approach enables quantitative molecular dynamics simulations with quantum electrons and nuclei for molecules at a fraction of cost of explicit AIMD calculations, thereby allowing to achieve unprecedented insights into (thermo)dynamics of molecules [1,2].

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Magic with Semiconducting 2D Nanolayers

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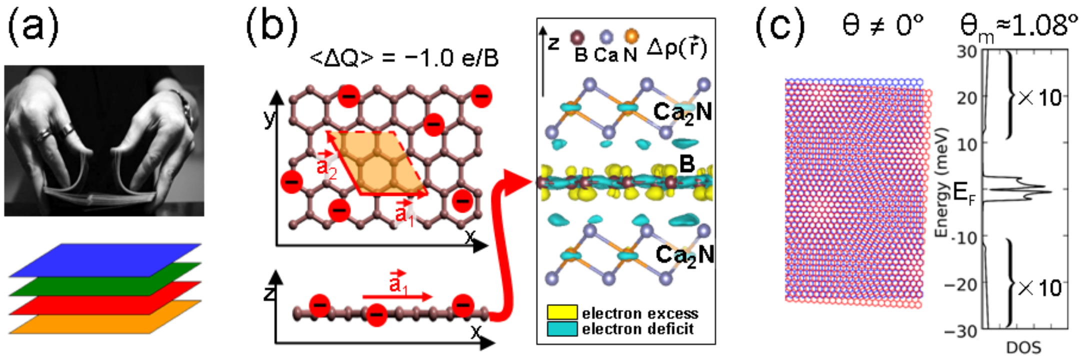

Figure 1: (a) Card magic illustrating the van der Waals assembly of 2D materials to a functional nanostructure. (b) Conversion of a 2D boron monolayer to a honeycomb lattice due to electron doping provided by a 2D electride. (c) Unusual changes in the electronic structure of twisted bilayer graphene near the magic twist angle $\theta_m \approx 1.08°$.

Like in a magic trick, atomically thin layers of specific materials can be mixed and stacked in a well-defined way. Due to the inter-layer interaction and charge transfer, the heterostructure may exhibit sometimes unexpected behavior. This occurs in the case of elemental boron, which is notorious for a large number of stable allotropes not only in 3D bulk, but also in 2D. We find that a previously unknown 2D ε–B allotrope converts stepwise to a stable honeycomb structure when doped with electrons, resembling a magic conversion of boron to carbon atoms that carry one more valence electron [1]. As seen in Fig. 1(b), sufficient extra charge to initiate this transition may be provided when 2D boron is brought into contact with the 2D electride Ca_2N. A different apparent example of magic involves the previously overlooked twist degree of freedom in 2D structures like bilayer graphene, which changes the Moiré pattern, as shown in the left panel of Fig. 1(c). Recent theoretical and experimental evidence suggests that the electronic structure near the Fermi level of twisted bilayer graphene (TBLG) depends extremely sensitively on the twist angle θ. Near the magic angle value $\theta_m \approx 1.08°$, a flat band emerges at E_F, separated from conduction and valence states by energy gaps. This unexpected behavior likely provides valuable insight into electron correlation and superconductivity in 2D systems. Even though TBLG and related non-periodic structures can not be treated by standard band structure theory, their electronic structure can be interpreted quantitatively using a parameterized model [2] that can be simply extended to consider also other deformations including shear [3].

This study was partly supported by the NSF/AFOSR EFRI 2-DARE grant number #EFMA-1433459.

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Magnetic tuning of ultracold chemical reactions: Theoretical insights

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Attaining external field control of bimolecular chemical reactions has long been a coveted goal of physics and chemistry. To explore how hyperfine interactions and magnetic fields can be used to achieve such control, we develop an extended coupled-channel statistical theory of barrierless atom-diatom chemical reactions, and apply it to the chemical reaction Li(^{2}S$_{1/2}$) + CaH($^2\Sigma^+$) $\rightarrow$ LiH($^1\Sigma^+$) + Ca(^{1}S$_0$) on a newly developed set of *ab initio* potential energy surfaces. We observe large field effects on the reaction cross sections, opening up the possibility of controlling ultracold barrierless chemical reactions by tuning selected hyperfine states of the reactants with an external magnetic field [1].
We also propose a new statistical approach to address the two central problems in ultracold molecular collision theory: (1) slow basis set convergence of molecular scattering observables and (2) their extreme sensitivity to the potential energy surfaces (PESs) underlying quantum scattering calculations. Specifically, we show that the probability distributions that an observable is in a certain range of values can be obtained by averaging the results of scattering calculations with much smaller basis sets than required for calculations of individual scattering cross sections. Moreover, we show that such distributions do not rely on the precise knowledge of the PES, making it possible to probabilistically predict experimentally relevant observables for a wide variety of molecular systems, currently considered out of reach of quantum dynamics theory [2].

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Expanding the horizon of automated metamaterials discovery via quantum annealing

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Complexity of materials designed by machine learning is currently limited by the inefficiency of classical computers. We show how quantum annealing can be incorporated into automated materials discovery and conduct a proof-of-principle study on designing complex thermofunctional metamaterials consisting of SiO2, SiC, and Poly(methyl methacrylate). The difficulty of this black-box optimization problem grows exponentially in the number of variables. Our quantum-classical hybrid algorithm consists of a factorization machine, an atomistic simulator, and a D-Wave 2000Q quantum annealer. Apart from the computational time needed for simulation, quantum annealing reduced the processing time to near zero regardless of the problem size. Our method was used to design complex structures of wavelength selective radiators showing much better concordance with the thermal atmospheric transparency window in comparison to existing human-designed alternatives. This result shows that quantum annealing can be used effectively in real-world design problems and indicates the direction of further applications.

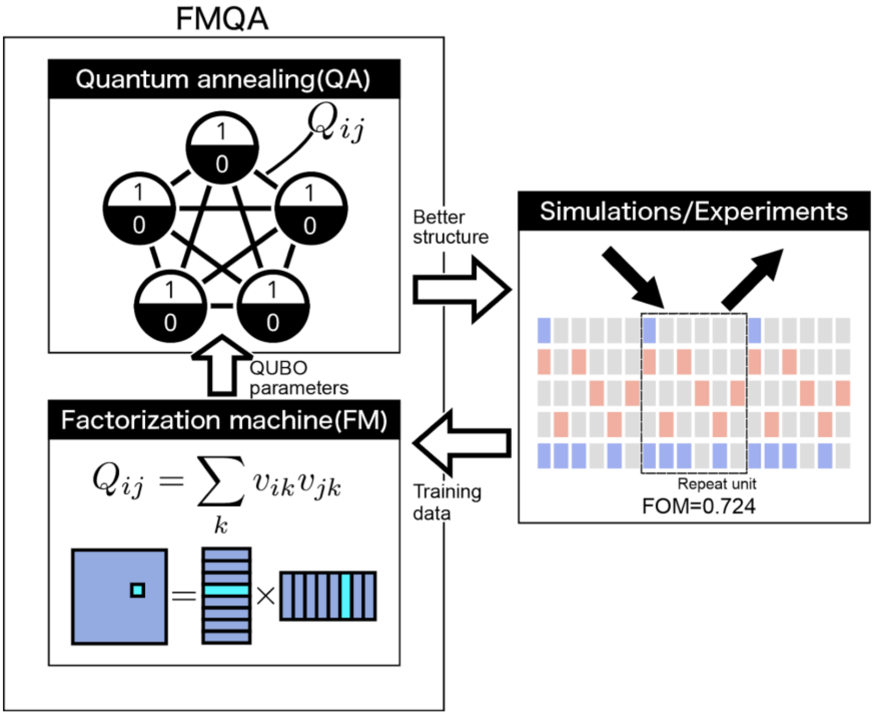

Figure 1: Procedure of our automated materials discovery using a factorization machine (FM) for learning and a quantum annealer (QA) for selection. Target property is the figure-of-merit (FOM) for the radiative sky cooling, which is evaluated by the rigorous coupled wave analysis (RCWA).

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A path-integral sampling (trajectory-free) approach to the calculation of quantum time correlation functions

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One of the major outstanding challenges in computational chemistry is the calculation of thermal quantum time correlation functions in condensed phases. Of the methods most commonly employed, semi-classical approaches generally require the generation of a very large number of trajectories with a high associated computational overhead. Alternatively, the accuracy of popular centroid[1] and ring-polymer[2] MD algorithms often satisfactory for linear operators under the appropriate conditions but degrades for non-linear operators, and routes to systematic improvement of these methods are not obvious. In this talk, I will introduce a scheme for approximating quantum time correlation functions numerically within the Feynman path integral formulation[3]. Starting with the symmetrized version of the correlation function expressed as a discretized path integral, a change of integration variables, often used in the derivation of trajectory-based semiclassical methods, is introduced. In particular, a transformation to sum and difference variables between forward and backward complex-time propagation paths. It can be shown that a formal integration over the path-difference variables yields a function of the path-sum variables that can be shown to be positive definite, thereby allowing the problem to be formulated as a sampling problem in the path-sum variables. The manner in which this procedure is carried out results in an open-chain path integral (in the remaining sum variables) with a modified potential that is evaluated using imaginary-time path-integral sampling rather than requiring the generation of a large ensemble of trajectories. Consequently, any number of path integral sampling schemes can be employed to compute the remaining path integral, including Monte Carlo, path-integral molecular dynamics, or enhanced path-integral molecular dynamics. This approach constitutes a different perspective in semiclassical-type approximations to quantum time correlation functions. As a practical approximation to the path-difference variable integrals, the potential is expanded in powers of these variables and the integral is performed analytically. The scheme is compared to the ring-polymer MD[2] and thermal-Gaussian LSC-IVR[4] approaches for a handful of example problems. Other formal considerations for rate theory and electronic excitation spectroscopy will also be discussed.

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Quantum Hydride Transfer in Formate Dehydrogenase: Environment Reorganization, Coupled Primary and Secondary Hydrogen Motions, and Kinetic Isotope Effects

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We present a new theoretical and computational framework for the simulation of enzymatic hydrogen-transfer reactions, here applied to the study of the hydride transfer step in Formate Dehydrogenase. The main features of our approach are the combination of a collective environmental coordinate adapted to QM/MM calculations, and an explicit quantization for the motion of the key light particles involved in the process. We find that in Formate Dehydrogenase the hydride transfer motion is coupled to the rearrangement of a secondary hydrogen atom. Depending on the donor-acceptor distance attained at the Transition State, the rearrangement of the primary and secondary hydrogen atoms can take place via tunneling through a potential energy barrier (nonadiabatic regime) or without an effective potential energy barrier (adiabatic regime). To calculate the reaction rate constant, we used a general theoretical framework that considers both adiabatic and nonadiabatic contributions. The calculated primary and secondary Kinetic Isotope Effects compare well with experimental determinations, supporting our simulations and approach. Our results show that the Kinetic Isotope Effect value strongly depends on the Transition-State donor-acceptor distance, and can thus be used as a sensitive probe of Transition State geometry changes. The approach and method presented here can be generalized to study other enzymatic proton- and hydride-transfer reactions. The combination of an adequate collective environment coordinate and the quantization of participating light particles, together with an appropriate theoretical framework, improve the understanding of quantum effects in these enzymatic reactions, and show how they are modulated by the protein structure through the selection of the donor-acceptor distances attained at the TS.

Semistochastic Heatbath Configuration Interaction Method and Orbital Optimization

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The Semistochastic Heatbath Configuration Interaction (SHCI) method [1, 2, 3, 4] is a variant of Selected Configuration Interaction plus Perturbation Theory (SCI+PT) methods that have been used for over 45 years, starting with the CIPSI method. Two key innovations make it faster than other SCI+PT methods:

1. It takes advantage of the fact that the Hamiltonian matrix elements for double excitations depend only on the four orbitals whose occupations change to make the determinant selection in both the variational and the perturbative steps much faster.
2. It overcomes the memory bottleneck of the perturbative step by evaluating the perturbative energy correction using a 3-step semistochastic approach.

The method has been applied to challenging molecular systems with more than 2 billion variational determinants and trillions of perturbative determinants, and to the homogeneous electron gas using more than 30,000 orbitals.

The efficiency of the method depends in part on the choice of orbitals. I will describe work in progress on improving the efficiency of the orbital optimization.

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Computations of Small Physical Effects in Nuclear Magnetic Resonance

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Despite that NMR computations have become routine in much of modern spectroscopy, interesting physical NMR phenomena remain. I introduce four distinct topics.

1. *J*-couplings over van der Waals (vdW) bonds have been computed [1]. There has only been one direct and one indirect observation, for $J(^{129}\text{Xe-}^{1}\text{H})$ in pentane(*l*) [2] and ΔJ(Xe-Xe) in a zeolite [3], respectively. $J(^{129}\text{Xe-}^{3}\text{He})$ measured in a gas-phase co-magnetometer [4] can now be quantitatively calculated [5] involving the virial coefficient of relativistic *J*-coupling. $J(^{129}\text{Xe-}^{3}\text{He})$ is vast compared to the sub-nHz physics sought with co-magnetometers.
2. Increasing B_0-field strengths in modern NMR render its parameters [6] field dependent. Only for ^{131}Xe quadrupole coupling [7,8] has this been verified [8,9]. ^{59}Co shift in Co(acac)$_3$ is rendered B_0-dependent by low-lying d-d excitations [10]. The leading $O(B_0^2)$ non-linear response terms [11] are evaluated presently.
3. Nuclear magneto-optics (NMO) prospect sensitive optical detection of nucleus-specific data. Therein, light polarisation is altered by molecular electrons interacting with nuclear spins. The phenomena include nuclear spin optical rotation (expt. [12], theory [13]), its dichroism, spin- and quadrupole-induced Cotton-Mouton (CM) effects, as well as spin-CM in the presence of B_0 [14]. We predict nuclear spin-induced magnetochiral birefringence and dichroism, possible reporters of chirality via the difference of the refractive index for light propagating parallel and antiparallel to nuclear spin magnetisation [15].
4. In spin-exchange optical pumping, polarisation is transferred from optically polarised Rb to noble gas nuclei in gas [16]. We extract from molecular dynamics a large number of Rb-Xe interaction events, and analyse them using spin dynamics driven by quantum-chemical spin Hamiltonian [17]. We reproduce the roles of binary collisions and long-lived vdW complexes in the transfer and witness a step-wise build-up of ^{129}Xe polarisation upon vdW oscillations.

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Insights into chemiluminescence from molecular dynamics simulations and machine learning analysis

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Chemiluminescence is the emission of light as a result of a non-adiabatic chemical reaction [1,2]. One the simplest molecules with chemiluminescent properties is 1,2-dioxetane. While the yield of the chemiluminescent process is observed to be low in 1,2-dioxetane (0.3%), it increases to 35% by substituting the hydrogen atoms by methyl groups. The reason for this impressive increase has remained an outstanding question. Firstly, we address it using ground-state and non-adiabatic dynamics of the decomposition reaction [3,4]. The simulations show that methyl-substitution leads to a significant increase in the dissociation half-time. The molecular system stays longer in the so-called "entropic trap" region where a manifold of states are degenerate, and more population is transferred into the excited state of the product before dark decomposition occurs. A simple kinetic model is proposed (Figure 1A). While simulations are key to the understanding of chemical reactions, a current challenge is the in-depth analysis of the large amount of data produced, in order to provide valuable insight. Here, we present machine learning models trained to predict directly a specific outcome quantity of ab initio molecular dynamics simulations of chemiluminescent reactions (Figure 1B). Our results show that in order to make accurate predictions, the models evidence empirical rules that are, today, parts of the common chemical knowledge [5]. This paves the way for conceptual breakthroughs where machine analysis would provide a source of inspiration to humans.

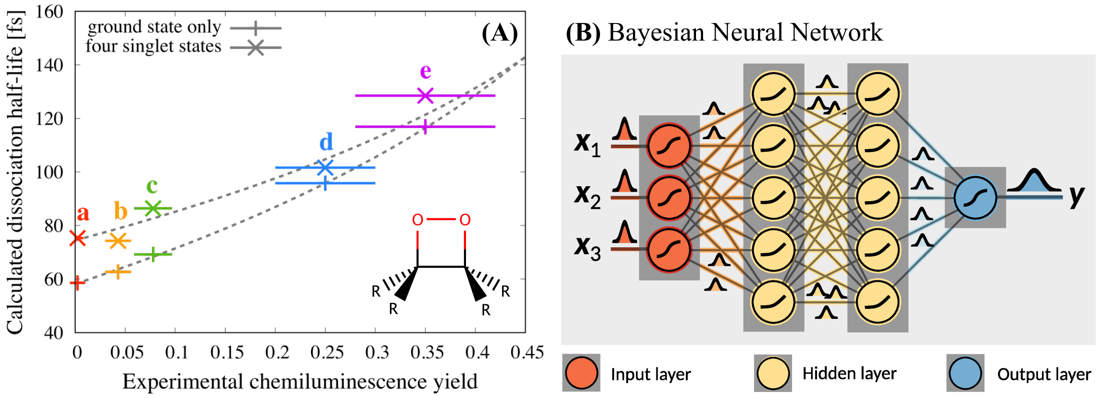

Figure 1: (A) Molecular dynamics simulations of the decomposition of 1,2 dioxetane. (B) Bayesian neural network trained to reproduce the molecular dynamics results.

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Spectra of O_2 induced by collisions with N_2 and O_2

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Collision-induced absorption (CIA) is the phenomenon that light is absorbed through the interaction between colliding molecules, even for transitions that are forbidden for the isolated molecules. CIA contributes to the atmospheric heat balance and is important for the electronic excitations of O_2 that are used for remote sensing. Moreover, absorption by O_2-O_2 pairs has been proposed as a biomarker to be observed in exoplanetary transit spectra.

The absorption spectra of the $X\,^3\Sigma_g^- \to a\,^1\Delta_g$ and $X\,^3\Sigma_g^- \to b\,^1\Sigma_g^+$ electronic transitions in O_2 are extremely weak, since these transitions are electric-dipole forbidden by both spin and spatial selection rules. Important additional absorption is induced by collisions with N_2 and O_2. We computed the O_2-O_2 and O_2-N_2 CIA spectra by *ab initio* electronic structure calculations of the relevant ground and excited state interaction potentials and the transition dipole moment functions, followed by diabatization and quantum mechanical scattering calculations [1,2,3]. We unambiguously identified the underlying mechanisms, which —contrary to textbook knowledge— are shown to depend explicitly on the collision partner: N_2 or O_2. This explains experimentally observed qualitative differences between O_2-O_2 and O_2-N_2 collision-induced spectra in the overall intensity, line shape, and vibrational dependence of the absorption spectrum. Moreover, we provided explicit analytical expressions for the spectral line shape depending on the underlying mechanism, which can be applied in the calibration of satellite spectrometers that probe various greenhouse gases or pollutants in the atmosphere [4].

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Benchmarking GW for quantum chemistry applications

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For many years, computational limits have forced *GW* calculations to employ approximations without the possibility to systematically evaluate their validity. In such a situation, the search for accuracy and precision can become very challenging, up to the point where one risks sacrificing precision for the sake of accuracy. With increased computational resources, this situation is changing but performing fully converged none approximated GW for solids is still a big challenge. For finite size systems, however, calculations can be more tractable.

In this contribution I summarize the results of the *GW*100 project. The *GW*100 set is a benchmark set of the ionization potentials and electron affinities of 100 molecules computed using the *GW* method using different independent *GW* codes and different *GW* methodologies. The quasi-particle energies of the HOMO and LUMO orbitals are calculated for the *GW*100 set at various levels of approximations. The use of different codes allows for a quantitative comparison of the type of basis set (plane wave or local orbital), handling of unoccupied states, the treatment of core and valence electrons (all electron or pseudopotentials), the treatment of the frequency dependence of the self-energy (full frequency or more approximate plasmon-pole models), and the algorithm for solving the quasi-particle equation.

At present 10 different codes have contributed to the project resulting in over 35 data sets. At *G*0*W*0@PBE level very tightly converged results obtained with very different codes, including fully analytic *GW*, answer the question on precision. A comparison of six different levels of self-consistency in *GW* to reference values calculated at CCSD(T) level of theory answers the question on accuracy.

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https://gw100.wordpress.com/papers/

Linear scaling DFT accelerated with GPUs and ML

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Linear scaling density functional theory with a demonstrated capability to simulate millions of atoms has been available for a couple of years in CP2K.[1] With increasing computer resources and refinements in algorithms, such simulations have become quite feasible. With tight-binding basis sets on workstations, with DFT quality basis sets on supercomputers. This progress is enabled by software, in particular a library for sparse matrix matrix multiplication. This enabling library, DBCSR, is now stand-alone and freely available.[2] It is highly efficient, MPI parallel, threaded and GPU-accelerated.[3]

Recently, the challenge of generating optimal, domain specific GPU kernels has been tackled with a combination of just-in-time (JIT) compilation and machine learning (ML). We show how ML parameters reach near optimal performance for 10000s of possible kernels.[4] Finally, we discuss how machine learning can be used to construct adaptive basis sets. This technique is based on the intuitive observation that an optimal basis set must adapt to its atomic environment. This optimal adaptation can be inferred from available data. This technique allows for large speedups (up to 50x), essentially allowing DFT calculations at tight-binding cost.[5]

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Systematic development of small molecules to inhibit amyloid beta aggregation in Alzheimer's disease

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Alzheimer's disease, which is the most common cause of dementia, affects over 50 million people worldwide. Among the top ten causes of death, this condition is currently the only one that we cannot prevent, cure or even slow down. In the last twenty years, great advances have been made in understanding the molecular origins of this disease, which, as we now know, is caused by the formation of abnormal protein aggregates in the brain of affected patients. Despite this knowledge, however, it has been extremely challenging to develop drugs capable of preventing the formation, or promoting the removal, of such protein aggregates. I will describe a novel drug discovery approach that has led to the discovery and systematic optimisation of compounds capable of blocking the key steps in the protein aggregation process.

Modeling Weak Interactions With Spherical Atomic Electron Densities

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Traditional force fields use a Lennard-Jones potential and point charges to model weak interactions in atomistic simulations, e.g. of biomolecules [1] or porous materials. [2] Such models involve numerous empirically adjusted parameters, which can be statistically estimated on a case-by-case basis. This is not only a daunting task, it is also difficult to guarantee *a priori* that such empirically adjusted parameters will be reliable in every use case, e.g. due to over-fitting. In order to limit the risk of over-fitting, we propose a new additive force field for weak interactions, whose primary objective is to contain as little as possible adjustable parameters. Our new model expresses intermolecular interactions in terms of integrals of electron densities of the non-interacting fragments, and is hence called the Monomer Electron Density Force Field (MEDFF). [3] The interaction energy comprises four terms in line with Symmetry-Adapted Perturbation Theory: electrostatics, exchange repulsion, induction and dispersion, of which the latter three MEDFF terms contain one linear adjustable parameter each. These parameters were fitted to SAPT/Aug-cc-pVTZ data for the S66x8 database of molecular dimers and were further refined to CCSD(T)/CBS energies of the same dimers. [4] MEDFF performs remarkably well for dispersion-dominated interactions, but due to its additive structure, it shares some typical weaknesses of non-polarizable force fields. MEDFF employs approximate electron densities, sums of spherical atoms, for the sake of computational efficiency. The spherical atoms are expressed as a sum of exponential density functions, at most one for each atomic shell, such that all integrals in MEDFF can be computed analytically at a typical force-field cost. The sum of exponential functions is derived from a reference electron density with the Minimal Basis Iterative Stockholder (MBIS) method. [5] As opposed to traditional density fitting, MBIS uses the Kullback-Leibler divergence as a loss function and it can therefore also be interpreted as a variant of the Hirshfeld partitioning method.

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Relativistic coupled cluster for a new generation of supercomputers

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I will present a new implementation of relativistic coupled cluster algorithms[1,2,3] that is based on the efficient GPU-adapted and parallel ExaTensor library of Lyakh[4,5]. I will discuss our design choices, required starting data, present capabilities and performance of the code. I will also give an outlook of our possible further developments. The code will be provided as open-source with the December 2019 release of DIRAC[6].

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Coarse-graining of Feynman Path Integrals in Statistical Mechanics

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The imaginary time Feynman path integral formalism for quantum statistical mechanics provides a way of understanding the nuclear quantum effects in complex condensed matter systems. Several numerical path integral based methods such as path integral molecular dynamics (PIMD), path integral Monte Carlo (PIMC), centroid molecular dynamics (CMD), and ring polymer molecular dynamics (RPMD) have been developed based on the quantum-classical isomorphism in which a completely classical "ring polymer" can be used to represent each quantum particle. We have recently been addressing two important problems in the area of path integral methodologies. First, despite the success of the previously mentioned numerical methods, path integral simulations are more computationally expensive than classical ones due to the presence of multiple quasi-classical "beads" in the isomorphic ring polymer. By combining the quantum-classical isomorphism and a systematic coarse-graining (CG) methodology, we have developed a many-body formalism of the coarse-graining of path integrals (CG-PI) approach and have devised a methodology based on the exact CG-PI theory called numerical CG-PI (n-CG-PI). Due to the CG representation of the ring polymers, which greatly decrease the number of degrees of freedom to be considered, it is shown that n-CG-PI can quantitatively capture the structural features of liquids compared against the exact PIMD results with only computational resources that an equivalent classical MD simulation would use. To expand on the many-body CG-PI theory work, we have also worked out a further refinement of the analytical CG-PI theory to include many-body interaction effects in the derivation. Additionally, a more sophisticated algorithm to numerically calculate the effective CG potential is currently being developed. The CG-PI theory, both in exact and approximate forms, further provides an important reductionist conceptual perspective to understand equilibrium quantum systems at finite temperature. A second project concerns the RPMD method, which seeks to approximate real time quantum dynamics. RPMD has been known to suffer from a "resonance problem" in which non-physical peaks appear in the RPMD calculated vibrational spectra. This arises when the frequencies of the higher order normal modes of the ring polymer are similar to those of the physical system, and it is an unphysical artifact of the method. To better understand the behavior of RPMD dynamics, we have carried out an analysis that utilizes the generalized Langevin equation (GLE). Such a formalism uses a familiar system-bath motif, and is shown to reproduce the general behavior of RPMD time correlation functions. The analysis also helps to explain why RPMD deviates from the exact quantum results for simple one-dimensional anharmonic oscillator systems.

NMR Shielding Tensors and Shifts in the Local Exact Two-Component Theory

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An efficient implementation of scalar-relativistic NMR shielding tensors based on the one-electron spin-free exact two-component theory (X2C) is presented [1]. It utilizes the finite nucleus model and takes advantage of the diagonal local approximation to the unitary decoupling matrix (DLU). This allows for routine calculations of large molecules with heavy atoms. Efficiency is demonstrated for heavy-element clusters and organometallic complexes with more than 120 atoms. The accuracy of the DLU scheme is evaluated based on NMR shielding constants and chemical shifts of C, O, Si, Ge, Sn, Xe, W and Pb. Further, extensions for the all-electron relativistic Karlsruhe basis sets [2] are presented. These extensions require at most four additional primitive basis functions. A large set of more than 250 closed-shell molecules was used to assess the quality of the developed extensions throughout the periodic table of elements.

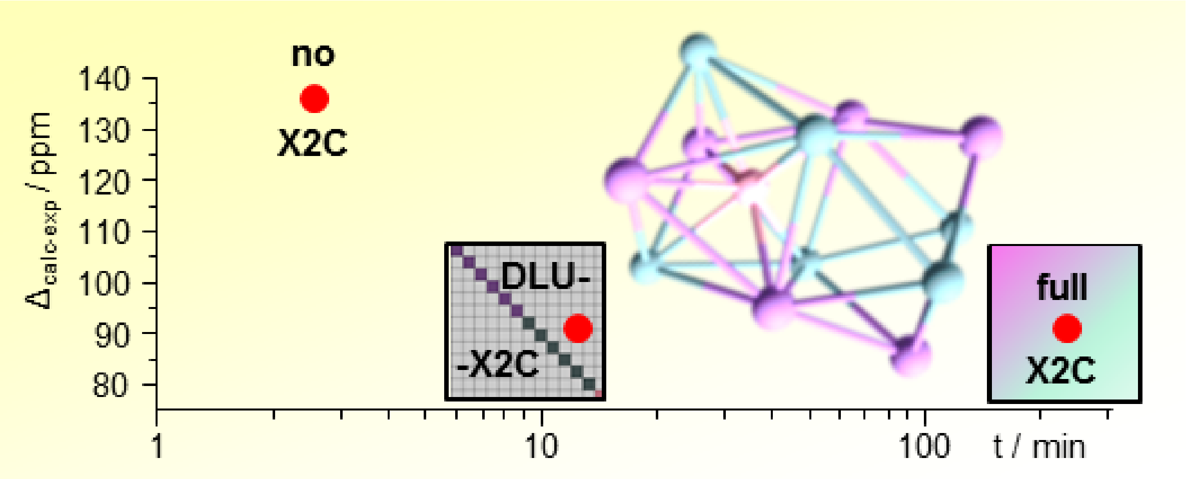

Figure 1: Accuracy and efficiency of DLU-X2C versus full X2C and non-relativistic treatment for Sn-119 NMR shifts in $[Co@Sn_6Sb_6]^{3-}$.

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Explicitly correlated local coupled-cluster methods for large molecules

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We review our recent developments of explicitly correlated local coupled cluster methods for closed-shell and open-shell molecules. The virtual space is spanned by pair-specific domains of pair natural orbitals (PNOs), and weak correlations of distant electrons are treated by accurate pair approximations. Basis set incompleteness errors as well as errors caused by the domain approximations are strongly reduced by explicitly correlated (F12) terms. The closed-shell PNO-LCCSD(T)-F12 method [1-4] has been applied for computing reaction energies of numerous difficult systems with up to about 300 atoms and 10000 basis functions [4]. The method is well parallelized, and on small compute clusters such calculations can be carried out in a few hours of elapsed time. For smaller systems, typical errors relative to the corresponding canonical CCSD(T)-F12 method amount to less than 1 kJ/mol for reaction energies; for larger systems the accuracy can only be estimated by studying the convergence with respect to the domain sizes, and this indicates that also in large systems the local domain errors can be reduced to well below 1 kcal/mol. Errors caused by the weak pair approximations are generally negligible. Intermolecular interaction energies have been computed for the S22, S66, and X40 test sets, and the root mean square (RMS) errors relative to the best previous calculations amount to less than 0.05 kcal/mol [5]. Recently, the method has been extended to spin-orbital based open-shell PNO-RCCSD [6], based on spin-free PNOs obtained by a spin-restricted MP2 method [7]. In open-shell cases the accurate treatment of single excitations turns out to be more critical than for closed-shell calculations, and various approximations are compared. The method has been applied for computing ionization energies and radical stabilization energies, and the accuracy is found to be very similar as for closed-shell calculations. An extension to open-shell PNO-RCCSD(T)-F12 is in progress. Finally, we give an outlook to the treatment of large strongly correlated systems using new CASSCF [8] and (multi-state) PNO-CASPT2 [9,10] implementations. All described methods are available in the MOLPRO quantum chemistry program (version 2019.3).

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Multisliced Gausslet Bases for Electronic Structure

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A major driver of the cost of density matrix renormalization group, tensor network, and quantum computing algorithms for electronic structure scale is the number of terms in the Hamiltonian. A conventional basis, for which the number of two electron terms scales as N^4, where N is the number of basis functions, are not ideal for these methods. Gausslets[1] are a new type of basis set, based on wavelet technology, which allow strictly diagonal two electron Hamiltonians, with the number of terms equal to N^2. Gausslets are smooth, highly local, orthogonal, and integrate like delta functions, giving them the diagonal property. In our multisliced gausslet formulation[2], they also have variable resolution, and can be combined with ordinary Gaussian bases. Here we given an overview of this technology, with applications to hydrogen chains using DMRG, comparing results with standard bases in the full-CI, complete basis set limit. In this regime, for hydrogen chains, multisliced gausslets can surpass Gaussian basis sets in accuracy, without relying on extrapolation in the level of completeness. We also report on our progress in extending the approach to more general molecules.

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Resolution-of-the-Identity and Beyond

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Achieving quantitative accuracy in the prediction of energetic and spectroscopic properties can become challenging as the size and complexity of molecules increase due to the accompanying rise in computational costs (i.e., computer time, memory, disk space). Developments by our group and applications that have provided insight about energetic predictions, the theoretical strategies used for the predictions (i.e., density functional approximations, and *ab initio* single and multi-reference strategies), and strategies for dramatically decreasing costs (i.e., resolution-of-the-identity, localization schemes) will be highlighted. Specifically, the correlation consistent Composite Approach (ccCA), which effectively has been utilized for many hundreds of main groups species, will be discussed, and its combination with routes for localizing and screening molecular orbitals have been considered. Recently, the domain-based local pair natural orbital methods (DLPNO) methods have been implemented within ccCA, and, here, the electronic energies, enthalpies of formation, and CPU times determined using ccCA, RI-ccCA, and DLPNO-ccCA are demonstrated for a set of 119 molecules consisting of first- and second-row main group atoms and linear alkanes. Several additional strategies are also discussed.

Simulating Non-adiabatic Photochemistry using Grids and Gaussians

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In this talk, methods to solve the TDSE will be presented showing how the dynamical behaviour of photo-excited molecules can be described. Quantum effects are often key due to strong coupling between nuclear and electronic motion when potential surfaces are close in energy, or cross at conical intersections and a both electrons and nuclei should be treated quantum mechanically for good results. A basic problem, still an area of active research, is solving the huge computational resources needed by accurate quantum dynamics simulations. This scaling manifests itself in two ways. Firstly in the computer resources required for the propagation of the nuclear wavepacket. Secondly in the space to be covered when calculating the potential energy surfaces.

The multi-configurational time-dependent Hartree (MCTDH) algorithm has gone a long way in solving the first problem [1]. In particular the multi-layer form (ML-MCTDH) is able to propagate multi-dimensional wavepackets with 100s of degrees of freedom. These grid based methods, however, in general require global potential surfaces which can restrict it to using model Hamiltonians rather than general, flexible molecular potentials. While this approach has been very useful in describing the initial stages of, e.g. non-adiabatic dynamics after photo-excitation [2] it is not able to describe the longer time photochemistry.

An approach to break both the exponential scaling and provide general potentials is the variational multi-configurational Gaussian (vMCG) method [3]. This uses a set of Gaussian wavepackets (GWP) as a time-dependent basis, but unlike conventional GWP methods, the GWPs follow variational rather than classical trajectories and retains the full quantum description of the system. It is also suited for direct dynamics simulations, calculating the potential on-the-fly using quantum chemistry programs and so opens up the use of flexible potentials [4]. The present state-of-the art of this method will be presented, showing its promise and highlighting the problems still to be solved.

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Toward Computational Design of Catalysts for CO_2 Selective Reduction via Reaction Phase Diagram Analysis

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Keywords: CO2 reduction, density functional theory, reaction phase diagram, selectivity trend, theoretical catalysis

Chemical conversion of carbon dioxide (CO_2) into value-added chemicals, for example, ethanol, has been recognized to be one of the most effective ways of carbon sources cycling. However, the selectivity controlling of CO_2 reduction is still a challenging problem due to the formation of a variety of products, such as methanol, methane, formic acid, and carbon monoxide, associating with complicated reaction mechanisms. Herein, a simple and effective theoretical analysis of "reaction phases diagram" to understand the selectivity of CO_2 reduction, based on the principle of reaction free energies with sequential priority is proposed. Using this principle, the fundamental understanding of the formation of different products in CO_2 reduction is rationalized. On the basis of reaction free energies' analysis, the selectivity trends of CO_2 reduction to methane, methanol, and ethanol from a number of experiments are discussed. At the end, the selectivity trends with a computer algorithm of searching full reaction pathways, explaining well the effects from catalyst sizes, substrate observed in experiments, are confirmed.

Finite temperature Green's function theories for periodic systems

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We perform periodic calculations with the Green's function second order (GF2) and GW method and discuss possible bottlenecks and remedies that can speed up these calculations. We evaluate momentum-resolved spectral functions and band gaps from bare and self-consistent second order perturbation theory for insulating periodic solids. We establish that, for systems with large gap sizes, both bare and self-consistent perturbation theory yield reasonable gaps. However, smaller gap sizes require a self-consistent adjustment of the propagator. In contrast to results obtained within a quasi-particle formalism used on top of bare second order perturbation theory, no unphysical behaviour of the band gap is observed. Our implementation of a fully self-consistent, -derivable and thermodynamically consistent finite temperature diagrammatic perturbation theory forms a framework on which embedding theories such as the dynamical mean field theory or self-energy embedding theories can be implemented.

Stereoelectronic control of π-nucleophilicity

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Nucleophilicity is a ubiquitous concept in chemistry. According to IUPAC, nucleophilicity may be defined as the kinetic affinity of a Lewis base towards a common substrate, mainly involving the formation of a bond with a carbon atom. Whereas the electrophilicity is a well-defined concept, the achievement of a universal nucleophilicity model within the so-called conceptual density theory remains elusive.[1] Distortion-interaction analysis for the reaction of π-nucleophiles shown in Figure 1, reveals that the nucleophile-distortion energy smoothly varies from 1.6 to 2.4 kcal/mol across the studied series.[2] We herein present an alternative approach to measure this interaction energy, based on the Second Order Perturbation Theory Energies of interaction within the Natural Bond Orbital (NBO) framework, highlighting their stereoelectronic nature into a quantitative fashion. First, we estimate the electron-donor releasing ability of alkyl groups towards the electron-rich π-bond in both the TS region and reactants stage by computing the corresponding $\sigma_{C-H} \longrightarrow \pi^*_{C-C}$ and $\sigma_{C-C} \longrightarrow \pi^*_{C-C}$ stabilizing interactions. Thus, and in analogy with the distortion-interaction model, the difference between the corresponding $\Delta E^{(2)}$ of TS structure and reactants leads to the stabilizing interaction energy.

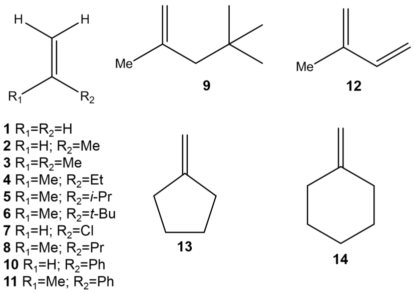

Figure 1: Structure of different π-nucleophiles analyzed.

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Quantum Chemistry Property Surface and machine learning in magnetic resonance relaxation modelling

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Interpretation of relaxation measurement can provide valuable information in chemistry, materials science and medicine for determining molecular structures, monitoring structural transformations, diagnostics and in probing dynamics at timescales relevant for biological systems [1]. Considering a long-lived nuclear singlet states (LLS), where a two-spin system is entirely correlated, have been shown to exceed magnetization (T_1) by a factor of 50, opening for new experiments [2]. However, in employing an analytical model of the relaxation a conclusive understanding is often challenging to reach due to a large set of unknown parameters.

An alternative to analytical relaxation model is the explicit simulation of spin-Hamiltonian trajectories. The spin Hamiltonian is built from NMR tensors that contain detailed information about the microstructure and dynamics of the samples. Accessible from first-principles quantum-chemical (QC) methods, the system-specific information is contained in the electronic structure of the substance. The relaxation times (T_1,T_{LLS}) are related to how the spin system couples to its environment. With QC sampling of the trajectory produced by atomistic molecular dynamics, relaxation observable may be computed directly, without adjustable parameters [3]. However, for accurate estimates of NMR relaxation, a vast number of QC calculations are needed, sampling many degrees of freedom (DOF) including both the spin moiety and the surrounding solvent, which makes the approach prohibitively costly.

We will present how this computational-bottleneck is overcome with development of Machine-learning QC-property surface. Central is the high-dimensional model representation [4], to manage the DOF. Application to LLS-relaxation due to the so-called spin-internal motion [2,3] will be illustrated.

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Positron Annihilation With Quantum Monte Carlo

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Experimental use of positron annihilation spectroscopy requires a strong theoretical background for drawing conclusions from the measurements and making a link between the atomic structures of the defects detected and the indirect information in the measured spectra. The most widely used method for making theoretical simulations of positron annihilation is density functional theory (DFT) [1]. While it is proven to be highly practical, there is demand for more accurate methods. This is why we have developed a Quantum Monte Carlo (QMC) [2] method for simulating positrons in solids. QMC does not require the approximation of multiple functionals, and it is able to sample directly two-body quantities, as well as expectation values in the momentum space. The trial wave functions are in a localized blip basis. With QMC, the electron-positron wavefunction is first optimized with variational Monte Carlo method (VMC), after which it is passed forward for the extremely accurate diffusion Monte Carlo simulation (DMC).

At the moment, we have obtained accurate predictions of the lifetimes of positrons in diamond phase-carbon and -silicon and wurtzite aluminium nitride. We are also studying correlation between electrons and a positron in the crystals as a function of location in real space by sampling enhancement factors, and examining how correlations play a role in annihilation events. In the future we may also simulate the Doppler broadening spectrum of annihilating electron-positron pair.

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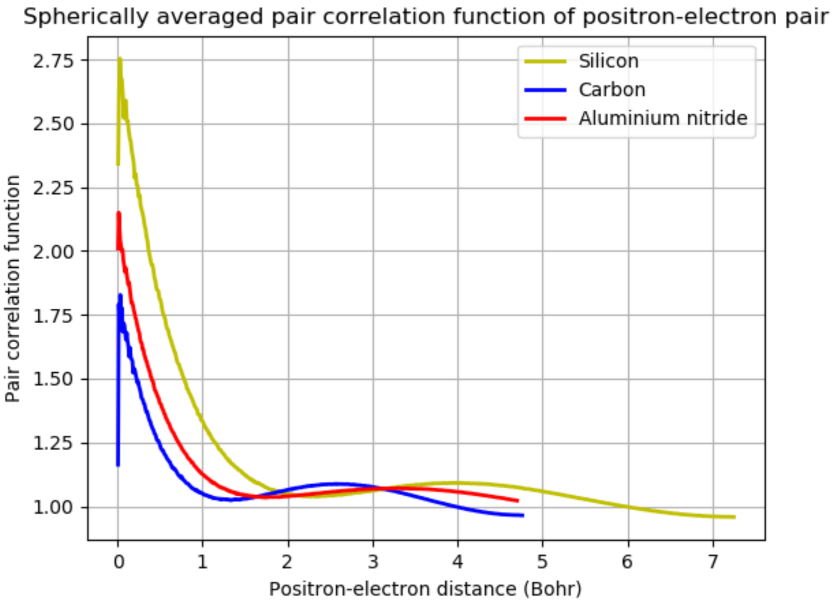

Allosteric regulation of the pH-dependent Ca(II)-binding affinity in langerin

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The dendritic C-type lectin receptor langerin plays an important role for the inert immune response of humans and other mammals. Through a high specificity towards mannose, it captures invading pathogens like e.g. HIV, to release them after endocytosis for degradation. For this purpose, the protein needs a calcium(II)-cofactor. The binding affinity to this cofactor is pH-dependent and already sensitive for a change from 7 to 6. The calcium binding pocket is, however, formed by aspartic and glutamic acids, which are not significantly protonated at pH 6. So the question is, how the observed sensitivity of the calcium binding is regulated. In a mutational study the side chain of a histidine (H294) was identified before as a partial pH-sensor, which is interesting because there is no direct contact with the binding-site. Thus, the effect of the additional proton has to be transported via an allosteric mechanism. We aim on explaining this mechanism on the atomic level by the analysis of microsecond long molecular dynamics simulations of the involved langerin species in different protonation states. In particular we use kinetic Markov state modelling for the identification of relevant long lived protein conformations. Furthermore, we use steered-MD setups to simulate the calcium-cofactor release event.

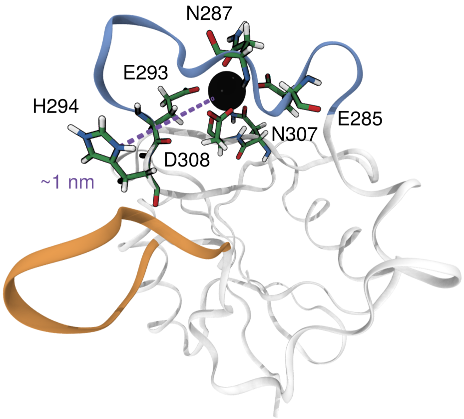

Figure 1: Structure of langerins carbohydrate recognition domain.

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Vibrational Spectroscopy of N_3^- in the Gas and Condensed Phase

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Abstract

Azido-derivatized amino acids are potentially useful, positionally resolved spectroscopic probes for studying the structural dynamics of proteins and macromolecules in solution. To this end a computational model for the vibrational modes of N_3^- based on accurate electronic structure calculations and a reproducing kernel Hilbert space representation[1,2] of the potential energy surface for the internal degrees of freedom is developed. Fully dimensional quantum bound state calculations[3] find the antisymmetric stretch vibration at 1974 cm^{-1} compared with 1986 cm^{-1} from experiment.[4,5] This mode shifts by 64 cm^{-1} (from the frequency distribution) and 74 cm^{-1} (from the IR lineshape) to the blue, respectively, compared with 61 cm^{-1} from experiment for N_3^- in water.[6] The decay time of the frequency fluctuation correlation function is 1.1 ps, in good agreement with experiment (1.2 to 1.3 ps)[7,8] and the full width at half maximum of the asymmetric stretch in solution is 18.5 cm^{-1} compared with 25.2 cm^{-1} from experiment.[6] A computationally more efficient analysis based on instantaneous normal modes is shown to provide comparable, albeit somewhat less quantitative results compared to solving the 3-dimensional Schrödinger equation for the fundamental vibrations. This model for N_3^- is then also used to characterize the dynamics around

Nonadiabatic dynamics with stochastic electronic structure forces

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Over the past several years, the present author has been concerned with several questions surrounding the feasibility of large-scale nonadiabatic dynamics calculations with *ab initio* forces. Briefly stated, these questions are: First, can we afford to do the dynamics (*i.e.,* can we reduce the cost of each molecular dynamics step) [1]? Second, are the states involved ordered properly (*i.e.,* as given by an affordable electronic structure theory) [2]? Third, can we afford to compute couplings between the states (*i.e.,* are analytical approaches available and implemented) [3–5]? Fourth, are the couplings physically sensible (*i.e.,* can they be corrected for spurious couplings that may arise from center-of-mass motion) [6]?

Together with co-workers from the Universities of Pennsylvania and Utah, we have provided affirmative answers to all of the above questions. Now I have turned my attention toward extending these successes to the range of stochastic electronic structure techniques that have come into use over the last decade, including full configuration-interaction quantum Monte Carlo methods and stochastic coupled-cluster approaches. In this poster, I will present some developments in this direction and indicate next steps.

In addition to the main scientific content given above, I may present letter-sized miniposters touching on other research in my group at the University of Texas Rio Grande Valley. Areas of interest include energy transfer following core excitation in the condensed phase, numerical methods for the determination of steric hindrance, and fundamentals & applications of nonadiabatic phenomena in mechanochemistry.

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Simulation of optical-pump Xray-probe NEXAFS spectroscopy to track photo-induced dynamics of organic molecules

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X-ray spectroscopy represents a versatile and powerful experimental toolbox for probing the dynamics of both core and valence electronic excitations, nuclear motions and material structure, with element and site specificity.[1-6] Following the achievements of a recent UV-pump X-ray probe time resolved NEXAFS (near-edge X-ray absorption fine structure) experiment,[6] in this contribution we explore the capabilities of this technique to track molecular excited state dynamics, providing complementary information with respect to the more widely employed optical spectroscopy.
The theoretical approach for the simulation of NEXAFS spectra, based on the multi-configurationl restricted active space self consistent field (RASSCF/RASPT2) method, is presented, and the *cis-trans* photo-isomerization of the azobenzene molecule is employed as a testbed case.[7]
Ground state and excited state NEXAFS spectra are computed on selected azobenzene molecular geometries (*cis*, *trans* and conical intersection(s) structures) as well as along the key isomerization coordinates. The origin of the simulated NEXAFS signals is explained, highlighting the specific signatures that make it possible to follow the excited state evolution from the Franck Condon point, towards the conical intersection(s).

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Ultrafast non-adiabatic dynamics in water clusters - hydronium radical as an intermediate in the formation of hydrated electron

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The ultrafast processes taking place in water clusters upon irradiation, and subsequent dissociation pathways following excitation have not yet been elucidated completely. The OH• radical along with the hydrated electron are the key species forming on femtosecond time-scales. Seemingly, when the photon energy is high enough the hydronium moiety forms and plays a significant role in these processes. [1] The results are complying with an experimental study performed along this theoretical study and a cooperative paper is in preparation.

We have performed a series of non-adiabatic *ab initio* molecular dynamics calculations on various-size water clusters and observed the reactivity on a femtosecond time scale. We observe two main dissociative pathways leading to either hydronium formation along with a solvated electron or to a hydrogen atom formation, which is a terminate step. We present an extensive study describing the reactivity of excited water clusters depending on the initial excitation energy and on the size of the water cluster.

The extensive study is supported with description of various-size hydronium-water clusters, their structure, their electron binding energies and the localization of an extra electron.

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Metal-ligand Complex Database as a Starting Point for Development of Metal-Protein Potentials

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Development of computationally accessible but sufficiently accurate potentials requires rich and consistent reference data. This work presents the construction of a database of metal-ligand complexes that serve as models for metal-protein interactions. The data is obtained using a DFT protocol combined with implicit solvation methods. The database combines several divalent metal-ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) with ligands representing amino acid side-chains in fixed geometries. Emphasis is placed on exploring combinations of ligands and their mutual orientations.

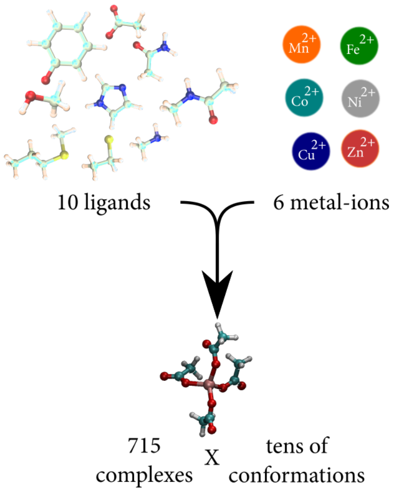

Figure 1: Target content of the database

We hope that the database could serve as a starting point for development of metal-protein potentials, validation of force-field parameters, and identifying which degrees of freedom need to be sampled more thoroughly, in order to capture the complexity of metal-protein interactions.

Parametrization and Evaluation of Transferable Minimal Pseudo-Potentials to Avoid Electrons Spilling-Out in Polarizable Embedded QM/MM Calculations

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Recently, the polarizable embedded QM/MM PE-ADC(2) method has been implemented to calculate electronic excited state energies and molecular gradients in complex molecular environments [1]. Comparing to full-QM ADC(2) much more costly calculations, the PE-ADC(2) can deliver reasonable accuracy for excitation and fluorescent emission energies, excluding the cases with significant electron density leackage to the MM subsystem. A remedy for electrons spilling-out issue is to supplement MM sites with pseudo-potentials that approximate the effect of Pauli repulsion. In this study, we have parametrized a set of effective core potentials ECPs, comprised of only one pseudo-potential function for each angular momentum that are representing all electrons of the isolated atoms based on some energetics criteria. These optimized pseudo-potentials are used in the PE(ECP)-ADC(2) calculations to compute the excitation energies for a test set with different type of excitations and various embedding environments. It will be shown that the PE(ECP)-ADC(2), compared to full-QM PNO-ADC(2), improves the accuracy particularly for the cases that diffuse basis sets are used.

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Wavelength dependent photochemistry via semiclassical dynamics

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Ab initio photodynamical simulations are gradually becoming a mature field, allowing for a routine simulations of light-induced processes in medium sized molecule. Theoretical treatment of photochemical reactions is typically based on semiclassical simulations, non-realistically assuming vertical promotion of initial vibrational wavefunction. Experimentally, molecules are typically excited with a light of a well defined wavelength. In fact, photochemistry is often controlled by the wavelength of light. For instance, molecules of photoswitches are able to change their conformation based on the light's energy, ultimately allowing us to control large molecular structures. Recently, there has been a Nobel price awarded for design of molecular machines, working on similar principle.

In this work, we show various applications of our new ground state nuclear density sampling method corresponding to a constant wavelength excitation. This method enables to generate structures from different regions of absorption spectra and thus to account for the experimental laser setup. We then proceed with subsequent semiclassical simulations, using methods like trajectory surface hopping (TSH) or Landau-Zener's (LZ) approach. Ultimately, we are able to interpret the results in terms of final quantum yields for various products.

So far, we were able to successfully apply this method to Freon-12 molecule[1] and faithfully reconstruct the experimental Cl fragment kinetic energy distributions. Currently, we explore so called photoinitiators - molecules, which create reactive species after interaction with light. Another task is to faithfully describe photochemistry of cyclopropanone. We discuss the difficulty of electronic structure calculations and the heavy influence of electron correlation.

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Beyond the LPNO-TCC: Introduction of DLPNO-TCCSD

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Coupled cluster (CC) methods tailored by matrix product state (TCC)[1] are highly accurate post-DMRG methods, which provide an accurate treatment of non-dynamic correlation with DMRG and dynamic correlation with CC framework. While being tremendously successful, canonical TCC method cannot handle large systems. Recently developed local variant of TCC (LPNO-TCC) is able to describe these systems and provide excellent results[2]. Unfortunately, due to the lack of proper linear scaling, calculations of very large systems is prohibitive even for LPNO-TCC. Therefore, one has to go beyond the LPNO-TCC.

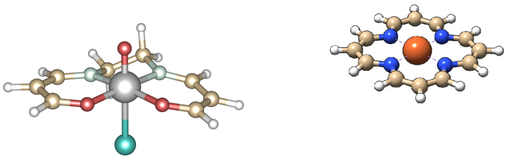

Figure 1: Studied systems.

In this poster, we present a benchmark of a novel domain-based local tailored coupled cluster singles and doubles method (DLPNO-TCCSD). We tested the performance of DLPNO-TCCSD on the rotational barrier of tetramethyleneethane, energetics of oxo-Mn(salen). iron porphyrin and model of NiFe hydrogenase with several different CAS spaces. These tests shows that DLPNO-TCCSD provides about 99.9% of the canonical correlation energy, which is a large improvement wrt. LPNO-TCCSD results, while being several times faster.

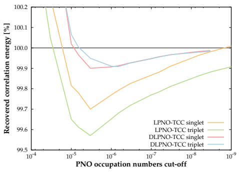

Figure 2: Comparison of DLPNO-TCCSD and LPNO-TCCSD.

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Observation of proton tunneling in hydrogen-bonded organic 1D molecular chains on Au(111)

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One-dimensional structures offer a rich ecosystem for realizing quantum states with potential application for advanced information technologies. Surface confined molecular self-assembly is one avenue for creating 1D systems, where the extant structure is controlled by the precursor shape, and functional group interlinking chemistry.

Here we study self-assembled 1D chains of zwitterionic molecule 2,5-diamino-1,4-benzoquinonediimines (DABQDI) [1] on Au(111) in ultrahigh vacuum at 5K using combined scanning tunneling and non-contact atomic force microscopies (STM/ nc-AFM) supported by theoretical analysis. Sub-molecular resolution achieved with a CO-functionalized tip hints structural information, specifically regarding the hydrogen bonds linking the precursor units.

To study how this proton tunneling we are using QM/MM techniques [2] to calculate the free energy barrier of the proton transfer at different temperatures. This free energy profile reveals a decreasing barrier with lower temperatures due to the reductions of the vertical movement of the atoms. We also study with Path Integral Molecular Dynamics [3] the proton transfer revealing a deep tunneling regime and a cooperative effect in the proton transfer.

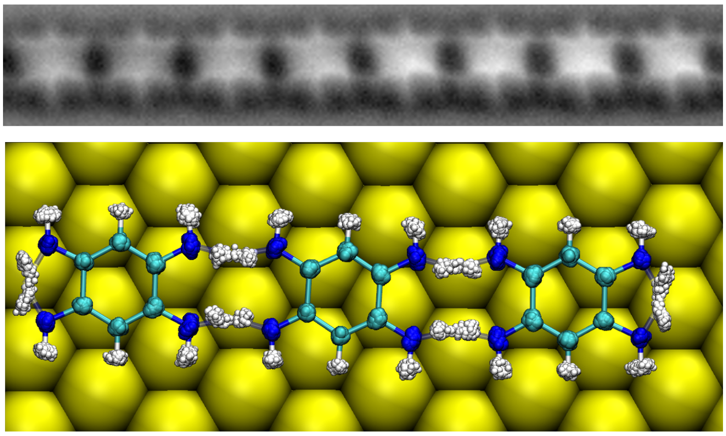

Figure: experimental images of the hydrogen bond chain and the transition state of the proton transfer with PIMD.

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The Arabidopsis (ASHH2) CW domain binds monomethylated K4 of the histone H3 tail through conformational selection

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Chromatin post-translational modifications (PTM) are thought to be important for epigenetic effects on gene expression. Methylation of histone N-terminal tail lysine residues constitutes one of many such modifications, executed by families of Histone Lysine Methyltransferase (HKMTase). One such protein is ASHH2 from the flowering plant Arabidopsis thaliana, equipped with the interaction domain CW and a HKMTase domain, SET. The CW domain of ASHH2 is a selective binder of monomethylation at Lysine 4 on the N-terminal tail of histone H3 (H3K4me1) and likely helps the enzyme dock correctly onto chromatin sites [1]. The study of CW and related interaction domains have so far been emphasizing lock-key models, possibly missing important aspects of histone-tail CW interactions. We here present an analysis of the ASHH2 CW:H3K4me1 complex using high-resolution NMR spectroscopy and molecular dynamics. ASHH2 CW emerges as a flexible domain that undergoes stabilization and compaction upon ligand binding. β-augmentation and a rearrangement of coils coincides with changes in the flexibility of the complex, in particular its coils but also in the β1 and β2 strands and the C-terminal part of the ligand. Overall, the binding process is consistent with conformational selection. We propose that this binding mode presents an advantage when searching out the correct PTM state among the highly modified and flexible histone tails, and also that the binding shifts the catalytic SET domain towards the nucleosome.

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Effective Fragment Potentials for non-rigid fragments

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The Effective Fragment Potential (EFP) method is a computationally accurate and efficient way to describe intermolecular interactions in condensed-phase systems. EFP is a model potential that decomposes non-covalent interaction energy into electrostatic, polarization, dispersion, and exchange-repulsion components, all of which are directly derived from the first principles. Recently, we extended the EFP method to model non-covalent interactions in macromolecules and polymers such as proteins and DNA. However current EFP implementation is not suitable for large scale simulations due to its inherent limitation of representing effective fragments as rigid structures. Thus, the process of obtaining EFP parameters in a system with flexible degrees of freedom entails multiple sets of *ab initio* calculations and requires intensive computational resources. To circumvent this issue, we formulate a computational approach that can efficiently utilize EFP for flexible molecules, so called Flexible EFP. We demonstrate computational efficiency and accuracy of Flexible EFP on extensive examples of amino acid interaction energies and electronic properties of Flavin chromophore of the cytochrome protein.

The numerical instability in non-collinear DFT

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Spin density function theory (DFT) is a widely used method. In the traditional collinear approach, spin magnetization is defined as the z-component of spin density while in non-collinear approach as the norm of spin density. The non-collinear approach preserves correct spatial symmetry but suffers from numerical instability at points with vanishing spin. The instability can be treated perfectly for local density approximation (LDA) [1], but less satisfactorily for generalized gradient approximation (GGA) [2,3]. In this work, some efforts are made to deal with the numerical instability in non-collinear GGA .

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Towards a computational protocol for VCD spectra of cyclic peptides

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Vibrational Circular Dichroism (VCD) is a type of spectroscopy that can be used to investigate chirality and to obtain information about conformers of flexible molecules. The experimentally measured VCD spectra rely heavily on calculated spectra to extract this kind of information. In our work, we are developing a computational protocol that together with experiments can determine the absolute configuration of cyclic peptides. This type of spectroscopy is very sensitive to minor structural changes and a common way to find the relevant conformations is to use Molecular Dynamics simulations. In our work we are testing a different approach for the conformational search; CREST developed by Grimme *et. al*. which uses a semi-empirical quantum chemistry method (GFN2-xTB) in combination with meta-dynamics.[1] The method has been tested for NMR spectroscopy and we are exploring its use for VCD.

When the protocol is found reliable, it will be used as a tool to determine the absolute configuration of cyclic peptides that are shown to be promising antibiotic candidates by the DigiBiotics project.[2]

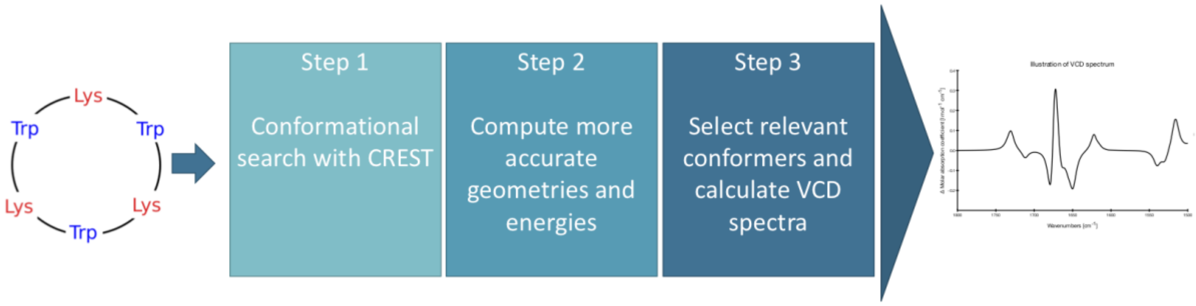

Figure: Overview of the protocol - An example of an interesting cyclic peptide consisting of the two amino acids Lysine (Lys) and Tryptophan (Trp), a summary of the three steps of the protocol and an illustration of how a VCD spectrum can look.

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QM/MM calculation of formic acid in argon matrix

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We present results of QM/MM calculation of formic acid in argon matrix. Including site structure for both conformers,trans and cis, and present IR-spectrum and compare it to experimental spectrum [1]. We also discuss how different argon-formic acid potentials affect the results and present a program that allows easy calculations of custom potentials.

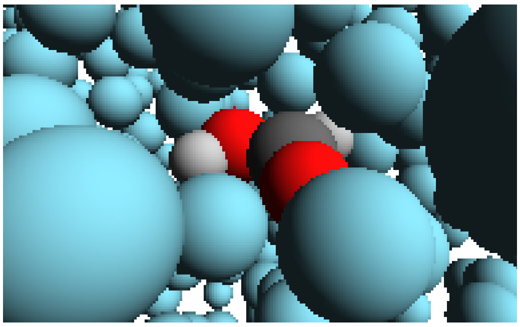

Figure 1: Formic acid in argon matrix.

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Calculation of Molecular Properties Using Relativistic Real-Time TDDFT

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The development and the scope of applications of relativistic real-time time-dependent density functional theory (RT-TDDFT) as implemented in quantum chemistry computer program `ReSpect` is presented.

The defining feature of RT-TDDFT is direct stepwise propagation of one-electron density matrix in time and on-the-fly evaluation of molecular properties. In contrast to the more widespread response theory approach, RT-TDDFT allows to access spectra in various regions, including near-resonant frequencies, from a single run, and does not require the evaluation of response kernels. The presented *relativistic* implementation is based on two Hamiltonians. First is the four-component Dirac–Coulomb Hamiltonian in the basis of restricted kinetically balanced Gaussian type functions exploiting the noncollinear Kramers unrestricted formalism. Second is the two-component quasirelativistic X2C Hamiltonian, obtained from the original four-component Hamiltonian by a decoupling transformation formulated entirely in matrix algebra. The former represents the fully relativistic description while the latter achieves 7-fold acceleration practically without the loss of accuracy and is thus well suited for treatment of larger molecules.

The molecular properties calculated with relativistic RT-TDDFT include the electron absorption spectra from UV/Vis [1] to X-ray [2] regions, circular dichroism spectra [3] as well as molecular hyperpolarizabilities [4]. The considered systems range from smaller benchmark systems to lanthanide compounds and heavy metal complexes.

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Geometry Optimizations with Quantum Monte Carlo

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Computing excited states is highly demanding for electronic structure methods, which often struggle to ensure high accuracy. We will work in the alternative framework of quantum Monte Carlo methods which use stochastic algorithms to solve the Schrödinger equation, scale well with system size, and offer a balanced description of the ground and electronic excited states. In this work we are using the real-space methods variational (VMC) and diffusion Monte Carlo (DMC).
First, the analytical expression of the variational-drift approximation[1] for DMC has been implemented in CHAMP and its limitations and possibilities are explored. Second, a stochastic process with a stability property is utilized by subjecting two close trajectories to the same random noise which allows for the accurate calculation of forces with a low dependence on the trial wave function.[2] Finally, we will accelerate the computation of interatomic forces required to determine optimal structures and reaction pathways, by exploring existing and developing new improved estimators characterized by small fluctuations and reduced systematic error based on the zero-variance zero-bias principle[3] which allows to extend these properties to forces. The advantage are considerably shorter Monte Carlo simulations and equally accurate structures.

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Improving DFT by Quantifying Density Errors

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Density Functional Theory (DFT) is one of the widely used methods for calculating chemical, physical, and electronic properties, and various approximate exchange-correlation (XC) functionals using the Kohn-Sham scheme have been developed and utilized. Clearly, DFT results are highly dependent on the XC approximation. In particular, the approximated XC functional has the self-interaction error unlike the highly accurate values from a high-level calculation such as QMC which requires a large amount of computation even for a small system. Energy errors caused by these functional approximations can be divided and investigated as the functional error and the density-driven error.[1] However, analyzing the two errors individually requires the exact XC functional and density, which is a formidable task. Recently, we devised the density-sensitivity as a practical way to provide an insight into density-driven errors and have shown that it works reasonably well for various calculations.[2] In this presentation, we demonstrate that density-sensitivity can be used to predict the need for density correction in the system of interest and to obtain dramatically improved DFT results using density-corrected DFT in the case of abnormal calculations.[3]

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Evaluating the contribution of continuum electronic states to van der Waals dispersion interactions

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High level calculations have demonstrated that in the case of hydrogen atom around one-third of the atomic polarizability arises from the quantum mechanical fluctuations of atomic electrons into the continuum electronic states. Consequently, there would be a considerable contribution from continuum electronic states to van der Waals (vdW) dispersion interaction between atoms. This contribution is typically neglected due to the lack of continuum states in atomic models, e.g. quantum drude oscillators [1], which are widely used for evaluating vdW dispersion interactions between atoms in preceding studies [2, 3, 4]. In the present work, we model atomic systems with simple one-dimensional potentials possessing both bound and continuum electronic states. Then for two of such modeled atoms, we calculate vdW dispersion interaction from second-order perturbation theory. The results from our analytical and numerical investigations demonstrate considerable contributions from continuum states to vdW interaction between atoms. We also show that the results for hydrogen atoms are recoverable from the models in our work under certain conditions for interacting atoms.

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Implementing real-time propagation time-dependent density functional theory for computing electronic circular dichroism spectra of Ag clusters

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DNA-stabilized silver clusters (Ag:DNA) and ligand-protected silver (LPAg) clusters have rapidly attracted interests due to their potential applications in wide range of nanotechnology, such as sensors and fluorescent imaging [1-2]. For these Ag clusters comparing experimental and computed electronic circular dichroism (ECD) spectroscopy is a very accurate indirect approach for probing structural properties, which are normally difficult to directly measure using X-ray techniques [3-5]. Accurate prediction of ECD spectrum for Ag:DNAs and LPAgs requires computing a large number of excited states. It may be prohibitively costly within the linear-response time-dependent density functional theory (LR-TDDFT) framework [5]. Here we represent an efficient method implemented in GPAW for computing entire ECD spectrum simultaneously based on real-time propagation time-dependent density functional theory (RT-TDDFT) and linear combination of atomic orbitals (LCAO) [6-7]. We also included some test cases here to show the accuracy and efficiency of our method.

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Efficient and chemically accurate excited states with quantum Monte Carlo

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Abstract:

We demonstrate an efficient protocol to compute chemically accurate ground- and excited-state energies and structures with quantum Monte Carlo (QMC), where the determinant component of the typical Jastrow-Slater wave function is constructed in an automated fashion using a selected CI algorithm. For small, yet theoretically challenging molecular systems, we show that our scheme to select relevant determinants is reliable and transferrable, and surpasses the performance of a conventional active-space description even with extremely compact QMC wave functions. Furthermore, we can treat multiple states in a balanced manner and accordingly compute vertical excitation energies, relaxed excited-state geometries, and adiabatic excitation energies in excellent agreement with the corresponding high-level coupled-cluster values.

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Advancements for the three-legged tree tensor network

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Recently, we introduced the three-legged tree tensor network state (T3NS) [1,2]. It is a variational state and a natural extension of the matrix product state (MPS) used in density matrix renormalization group theory (DMRG). Its structure allows an efficient optimization of the wave function while enjoying more flexibility in representing the entanglement of the system than the linear MPS.

In this poster, we demonstrate the spin-adapted T3NS [2]. The implementation is freely available on github [3]. Just as for DMRG, exploiting the spin and molecular point group symmetries of the quantum chemical hamiltonian provide considerable speed-ups.
Not only conserved quantum numbers such as the total spin can be easily used in the T3NS but also non-conserved quantum numbers. We demonstrate this by executing seniority-restricted calculations. In these type of calculations only Slater determinants with a certain maximal amount of unpaired electrons contribute to the optimized wave function.
When optimizing the T3NS, the convergence is dependent on the used orbitals, the ordering of the orbitals on the network and the geometry of the network. We briefly touch on this and have an outlook on future research for the optimization of the geometry and orbital ordering itself.

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Simulating advanced excitation energy loss spectroscopies of molecular excitations

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Electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) is becoming an important technique in spatially resolved spectral characterization of optical and vibrational properties of matter at the nanoscale [1]. Very recently, a new device composed by nanoscale holograms [2,3] or electrostatic phase elements allows analyzing the single components of orbital angular momentum (OAM) by spatially separating them (Fig. 1, top). Such an OAM-sorter drastically enhances EELS as innovative double-dispersed spectroscopy experiments.

In this work [4], we modified the theoretical framework needed to describe conventional low-loss EELS experiments in STEM, introducing a TD-DFT description of the molecular systems. Our work paves the way to study electronic transitions in single chromophores or supramolecular aggregates and devise new experiments [4,5] for the analysis of these excitations (Fig. 1, bottom).

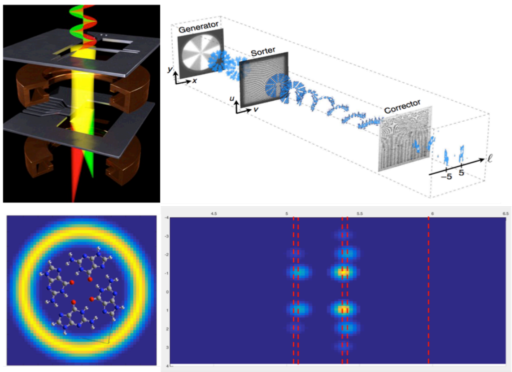

Figure 1: Top: scheme of the experimental apparatus of an electron beam carrying OAM. Bottom: TD-DFT simulation of OAM-resolved EELS experiment on a guanine-tetramer.

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Variational and cavity-free approach to solvation in a multiresolution analysis framework

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Most chemical systems of interest are in solution. Solvent models are therefore an important component of every quantum chemistry software. We successfully implemented a Self Consistent Reaction Field (SCRF) procedure for solving the Generalized Poisson Equation (GPE),

$$\nabla\left[\epsilon(\mathbf{r})\nabla V(\mathbf{r})\right] = -4\pi\rho(\mathbf{r}), \tag{1}$$

for a solvated system using a MW basis as outlined by Fosso-Tande and Harrison (2013). The dielectric function, $\epsilon(\mathbf{r})$, is defined as a functional of a cavity function which describes the values of the permitivity inside, outside and on the surface of the molecular cavity with a convenient sigmoidal shape.

We have also combined the GPE solver with the variational formulation of Lipparini et al.(2010). Our preliminary results look promising in terms of efficiency of the algorithm compared to a more traditional, nested SCRF approach.

This work is part of the ongoing development of MRChem: a multiwavelet code for all-electron DFT calculations

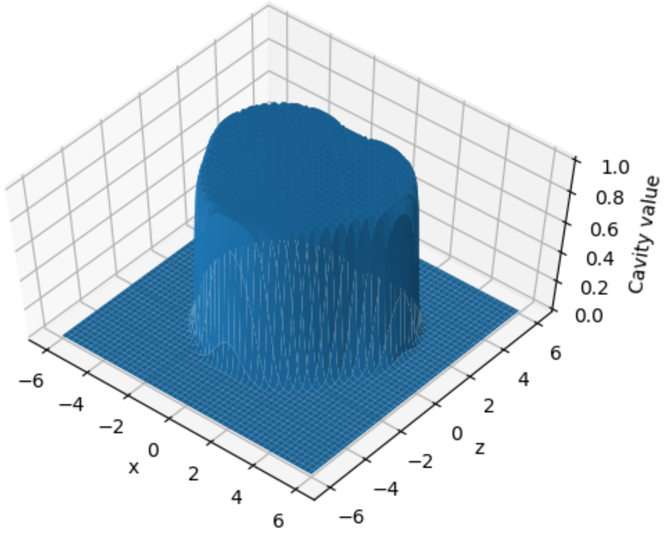

Figure 1: xz-section of a water cavity function. The z axis shows the function value $C = 0$ outside the cavity and $C = 1$ inside the cavity.

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Ab Initio Calculations for Spin-Gaps of Non-Heme Iron Complexes

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Heme and nonheme mononuclear iron oxygeneses and their synthetic analogues are known to perform a wide range of catalytic oxidative transformations in chemistry and biochemistry.[1] The most typical reaction is the C-H hydroxylation which has been proposed to be performed by an iron-oxo $Fe^{IV}=O$ active intermediate. The rate limiting step in these reactions was found to be the hydrogen atom abstraction process. These systems are also known for their multi-state reactivity. We have seen that many methods have problems with accurately calculating this reaction.[2]

Therefore, we have performed an extensive computational study of the quintet-triplet gap ΔE_{TQ} of a series of non-heme $Fe^{IV}=O$ species.[3] We employed our recently proposed multireference approach CASPT2/CC[4] to calculate the gaps and subsequently used these results to benchmark two variants of local coupled cluster approaches (DLPNO-CCSD(T) and LUCCSD(T0)). We have showed that current implementations of the local coupled cluster method are not sufficiently accurate. DLPNO-CCSD(T) systematically overstabilizes the quintet state by about 8 kcal/mol, whereas LUCCSD(T0) gives the too stable triplet ground state. Interestingly, we observed a good linear correlation between the ΔE_{TQ} values predicted by CASPT2/CC and DLPNO-CCSD(T). Therefore, a simple correction scheme, which significantly improves the accuracy of the latter method was proposed and validated. We have tested this correction on the calculation of the triplet-quintet gaps and on the example of the C-H activation reaction.

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DFT modeling of CO clathrate hydrates

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Clathrate hydrates (gas hydrates) are nanoporous crystalline solids composed of hydrogen-bonded water molecules forming cages within which gaseous molecules are encapsulated (see Fig. 1). Naturally present on Earth, gas hydrates can be observed on permafrost regions and on oceans floors, but also on comets and planets of the Solar System [1]. This natural occurrence makes them relevant for many geophysical and astrophysical applications.

Carbon monoxide (CO) hydrate might be considered an important component of the carbon cycle in the solar system since CO gas is one of the predominant forms of carbon. Intriguing fundamental properties have also been reported: the CO hydrate initially forms in the sI structure (kinetically favored) and transforms into the sII structure (thermodynamically stable) [2]. Understanding and predicting the gas hydrate structural stability then become essential. The aim of this work is, thereby, to study the structural and energetic properties of the CO hydrate using density functional theory (DFT) calculations. Performed on a complete unit cell (sI and sII), DFT-derived energy calculations lead indeed to the sII structure most thermodynamically stable. In addition, increasing the CO content in the large cages has a stabilizing effect on the sII structure, while it destabilizes the sI structure in agreement with recent experimental results [2,3].

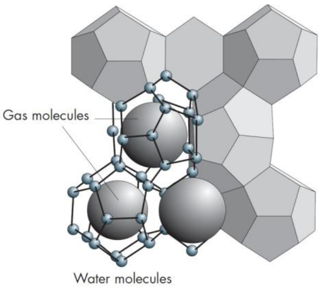

Figure 1: Clathrate hydrate

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Ring polymer path integrals as eigenvalue problem

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In ring polymer path integral methods an N-particle quantum system is mapped into a classical polymer ring, where the beads of the polymer are the replicas of the original N-particle system and they are connected through harmonic springs. This isomorphism is exact in the limit of infinite bead number. The equilibrium averages of the classical polymer give the corresponding thermal properties of the quantum mechanical system. [1]

We employed the transfer operator method for imaginary path integrals to calculate molecular partition functions. The transfer matrix approach is a handy technique in statistical physics that allows the analytical derivation of the partition function for some classical systems [2,3]. Due to this technique the calculation of the quantum partition function is transformed into an eigenvalue problem. This method has two main benefits: i) compared to the ring polymer molecular dynamics or Monte Carlo approximations the computational complexity of the partition function is independent of the applied bead number (replicas of the system) that means, this method can reach the exact quantum mechanical limit ii) in general case only the largest eigenvalue of the transfer operator is needed for the computation of the partition function. Moreover, we also derived an exact formula for the eigenvalues and eigenfunctions for the transfer operator of the harmonic oscillator.

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Construction of Diabatic Electronic States of Configuration Interaction type by Localization of Molecular Orbitals with Floating Occupations

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Diabatic states can be qualitatively defined as electronic states with a vanishing or weak dependence on the internal nuclear coordinates [1, 2]. In particular, they preserve a well defined character (i.e. charge distributions, bonding and nodal properties) thoughout the nuclear coordinate space of interest and represent a convenient tool to characterize the nature of the usual adiabatic electronic states, i.e. the eigenstates of the electronic Hamiltonian.

In this poster communication, we present a method to construct diabatic electronic states for a system that can be clearly separated into groups of atoms (the "monomers"). The method is based on two steps: (i) first, the relevant molecular orbitals (MO) are rotated to produce MOs localized on the monomers (LMO); (ii) next, diabatic reference states are built on the LMO basis and a set of adiabatic states of the system is transformed so as to achieve maximum overlap with the references [3].

In the first place the method was implemented in the framework of semiempirical Configuration Interaction based on Floating Occupation Molecular Orbitals (FOMO-CI) [4]. However, it can be applied without changes to ab initio wavefunctions, obtained for instance by state-average CASSCF or ab initio FOMO-CI [5].

We show how to employ the procedure to compute the low-lying diabatic states and electronic couplings involved in singlet fission [6] and exciton coupling for systems consisting of well separated chromophores. Moreover, we present a successful application of the method on the cis-trans isomerization in hexatriene, where the subsystems are covalently bound. Finally, we present the application of the algorithm to analyze adiabatic or time-dependent electronic wavefunctions obtained in excited state dynamics simulations.

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Coupled Cluster for Lanthanide Monofluorides

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The special properties of lanthanides make them promising for future applications. One of these attributes is the large magnetic moment stemming from the open f-shells resulting in strong magnetism of certain lanthanide based alloys. Another potential application, single molecule magnets, has gained interest in recent years[1]. The f-shells are quite compact and only weakly perturbed by the environment. Consequently, the optical transition involving these molecules only show minor influence of the environment. This is applied in laser crystals and also opens the path for exciting medical applications[2].
In this work we are taking a closer look at lanthanide monofluorides. On one side this has the advantage of only one internal coordinate. On the other side an oxidation state of +1 has a more complex orbital structure, than the more common oxidation states of +2 and +3. In a first step the potential energy curves were computed on the Hartree-Fock level using the average of configuration approach[3] and effective core potentials. We applied the core potentials developed by Dolg *et. al* for this oxidation state[4]. Based on this coupled cluster computation were performed using the DIRAC software package[5] and will be compared to available experimental and theoretical data.

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Rational Design of Nanosystems for Simultaneous Drug Delivery and Photodynamic Therapy by Multiscale Modeling

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Drug delivery systems are based on reversible interactions between carriers and drugs. Spacers are often introduced to tailor the type of interaction and to keep drugs intact. Here, we model a drug delivery system based on a functionalized curved TiO_2 nanoparticle of realistic size (700 atoms – 2.2 nm) by the neurotransmitter dopamine to carry the anticancer chemotherapeutic agent doxorubicin (DOX). The multiscale quantum chemical study aims at unraveling the nature and mechanism of the interactions between the components and the electronic properties of the composite system. We simulate the temperature effect through molecular dynamics runs of thermal annealing. Dopamine binds preferentially to low coordinated Ti sites on the nanoparticle through dissociated bidentate and chelate modes involving the diol groups. DOX is tethered by H-bonds, π-π stacking, dipole-dipole interactions and disper- sion forces. Comparing different coverage densities of spacer on the nanoparticle surface, we assess the best conditions for an effective drug transport and release: only at full coverage, DOX does not slip among the dopamine molecules to reach the nanoparticle surface, which is crucial to avoid formation of stable coordinative bonds with under-coordinated Ti atoms. Finally, given the strong absorption properties and fluorescence of DOX and of the TiO 2 photo- catalyst, we model the effect of light irradiation through excited state calculations to localize excitons and to follow the charge carriers life path. This fundamental study on the nature and mechanism of drug/carrier interaction provides solid ground for the rational design of new experimental protocols for a more efficient drug transport and release and its combination with photodynamic therapy.

Efficient Cysteine Conformers Search by a Bayesian Optimization Method

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Cysteine is a fundamental amino acid and has applications in different fields. In recent years, the conformers of isolated cysteine molecules have been widely studied with theoretical simulations and experimental methods [1,2,3,4], however, accurate cysteine conformers prediction with ab initio methods remains time-consuming and low efficiency. In order to do such search, several thousands starting structures needed be relaxed [2]. Here, we adopt a machine learning method based on Bayesian optimization combining with Density Functional Theory (DFT) [5] to search conformers of cysteine efficiently. In our new process, we only need 400 single-point energy calculations to find the global and local minimum structures. The tens of local minimum structures are further relaxed by DFT and corrected by vibration energy. Comparing to the previous studies, the energy order of six low-energy conformers predicted agrees with experimental results [1] and some new conformers have been predicted. This method can be easily extended to the conformer search of other molecules and nanostructures.

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Exploring photoinduced structural relaxation and solvation dynamics with multiscale simulations

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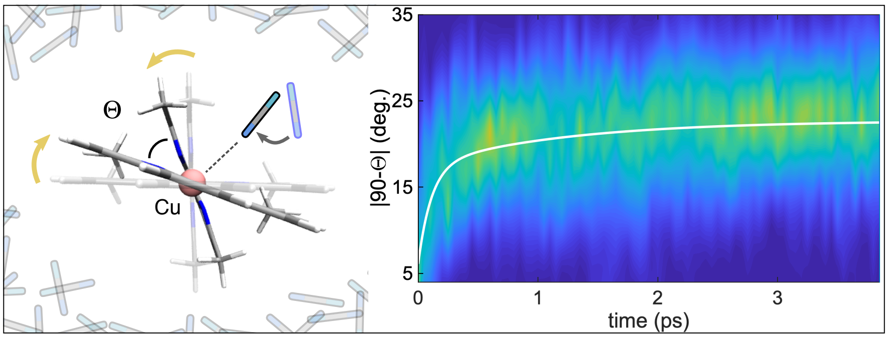
Efficiently harvesting solar energy using photoactive molecules requires a deep understanding of the transient structural changes after light excitation in solution. The excited-state relaxation can be influenced by many factors, most importantly the accompanying dynamical response of the solvent. Despite recent advances in ultrafast techniques, extracting a detailed picture of the instantaneous nuclear dynamics from time-resolved measurements in solution remains impossible without the support of atomistic simulations.
To address this challenge we have developed and implemented a multiscale quantum mechanics/molecular mechanics (QM/MM) Born-Oppenheimer Molecular Dynamics (BOMD) method [1] using a grid-based implementation of density functional theory (DFT) with a fast and robust description of excited states [2]. The methodology has been used to uncover highly elusive mechanisms of the ultrafast excited-state dynamics of photocatalytic transition metal complexes. We will show examples of these applications, ranging from predicting the vibrational relaxation and site-specific solvation dynamics following photoinduced bond formation in prominent bimetallic complexes for the interpretation of time-resolved X-ray scattering data [3,4], to resolving controversies regarding the solvent influence on the excited-state flattening of an archetype Cu photosensitizer [5].



QM/MM BOMD simulations of a prototype Cu(I) bis-phenanthroline complex reveal the coupling between the excited-state flattening dynamics, which controls the efficiency of photosensitization, and the intercalation of acetonitrile molecules between the ligands [5].

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Nuclear Spin-Induced Circular Dichroism: Using Nuclear Properties to Map Spatial Localization of Excited States

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Nuclear spin-induced circular dichroism (NSCD) is one of theoretically predicted nuclear magneto-optic effects [1]. NSCD occurs when the electron cloud is excited via a beam of light in the molecule with nuclear spins aligned along the direction of propagation of light. As has been theoretically shown, NSCD arises due to presence of localized interactions, such as paramagnetic spin-orbit coupling $\boldsymbol{h}^{\mathrm{PSO}}$ in the case of non-relativistic theory [1]. Thus, NSCD uniquely combines information about electron excitations with a highly spatially localized properties originating from atomic nuclei. It is of interest to understand how it relates to the molecular structure.

In the presented work we have explored how the spatial localization of the excited states affect the NSCD response of individual nuclei for different excited states [2]. We have used a computational protocol based on quadratic response function, which allows us to look at the NSCD response for different nuclei and each excitation. The results show that a strong NSCD signal for a particular nucleus and excitation can arise only if the nucleus is a part of a chromophore unit that is excited. This finding shows that NSCD could be used as an experimental tool for investigating the location and spatial extent of excited states within molecules.

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MFCC-PDE: Polarizable Density Embedding for large biomolecules

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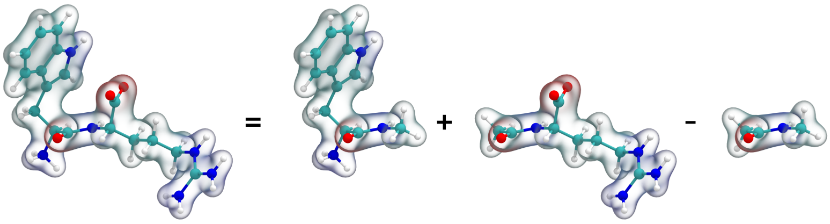
Polarizable Density Embedding[1,2] (PDE) is an extension of the well-established Polarizable Embedding (PE) model. The PDE model replaces the approximate multipole expansion in PE with exact quantum-mechanical electrostatics and further models non-electrostatic (Pauli) repulsion. Crucially, the inclusion of non-electrostatic repulsion solves the problem of electron spill-out[2] in QM/MM simulations. Both PE and PDE use the same classical description of polarization with a classical induced dipole model, which allows for a very efficient and accurate inclusion of the mutual polarization.

PDE has so far been restricted to treat solute-solvent systems, but we have now extended the model to cover much larger systems by applying a completely general Molecular Fractionation with Conjugate Caps (MFCC) strategy. The MFCC procedure is applied on a Fock matrix level

$$F_{\mu\nu}^{X} = \sum_{f=1}^{N_f} F_{\mu\nu}^{X,f} - \sum_{c=1}^{N_c} F_{\mu\nu}^{X,c}, \tag{1}$$

where X refers to the contribution from either the fragment density or repulsion operator. The resulting model, MFCC-PDE, is applicable to a wide range of systems, including proteins, DNA, lipids and supramolecular assemblies. MFCC-PDE is implemented in the Dalton program and is formulated within the general framework of response theory, which allows for the calculation of a wide range of molecular properties, e.g., excitation energies and multi-photon absorption strengths.



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Computational Chemistry and Organic Synthesis: Let Us Build a Bridge

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Progress in quantum chemistry and computational techniques allows chemists to understand and predict the outcome of organic reactions in a very efficient fashion. Hereby we demonstrate the power of bridging experiment and theory on some recent examples from our lab.

The Claisen rearrangement is a classical textbook reaction.[1] However, it still holds the potential to provide new experimental results and a series of novel Claisen-type rearrangements have recently been developed by the Maulide group.[2] Our combined theoretical/experimental study of these transformations reveals a diversity of possible pathways and products. The calculations clarify the experimental results and predict new reactions.[3]

The Maulide Group has also discovered a new synthetic approach leading to imidazoles with concomitant observation of an unusual sulfonyl migration.[4] Our in-depth theoretical analysis of possible intermediates and transition states shed more light on this rearrangement.

Moreover, some reactions can even proceed via several different unclear mechanisms. One of those examples is our TEMPO-mediated aminoxylation of ynamides.[5] The calculations explain the experimentally observed phenomena.

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Exact quantum dynamics for electron-phonon coupled systems with multi-set matrix product states

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Electron-phonon coupling is at the heart of many important phenomena in physics and chemistry, but challenges the applicability of analytical and numerical methodologies. We present a numerically exact method allowing to describe electron-phonon coupled quantum systems in their single-electron sector with unprecedented efficiency [1,2]. The approach is based on a tensor network decomposition applied to vibrational wavefunctions in a multi-set ansatz where the wavefunctions is expanded as a sum over products of electronic states and their associated vibrational wavefunctions. We apply our method to explore electron dynamics in the Holstein model in one and two spatial dimensions. The dynamics of (vertical) Franck-Condon excitations in the regime where Holstein-coupled vibrational modes mix strongly with electronic degrees of freedom is shown to sharply contrast with the known self-localized behavior of vibrationally relaxed excitations. Instead, the strongly-coupled modes are found to periodically induce resonances between interacting electronic sites, during which effective excitation transfer occurs, allowing Franck-Condon excitations to attain substantial mean square displacements under conditions where relaxed excitations are essentially trapped to a single site.

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Active Space Selection based on 1^{st} order perturbation Theory (ASS1ST)

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Efficient and robust approximations to the full configuration interaction (Full-CI) method such as the density matrix renormalization group (DMRG) and the Full-CI quantum Monte-Carlo (FCIQMC) algorithm allow for multi-configurational self-consistent field (MC-SCF) calculations with large active spaces. This opens up the possibility to treat large and complex systems that were previously untractable but at the same time it calls for an efficient and reliable active space selection as the choice of how many electrons and orbitals enter the active space is critical for any multireference calculation. In this work we propose an Active Space Selection based on 1st order perturbation Theory (ASS1ST)[1] that follows a 'bottom-up' strategy and utilizes a set of quasi-natural orbitals together with sensible thresholds for their occupation numbers. The required quasi-natural orbitals are generated by diagonalizing the virtual and internal part of the one-electron reduced density matrix that is obtained from strongly contracted n-electron valence perturbation theory (SC-NEVPT2) on top of a minimal active space calculation. Self consistent results can be obtained when the proposed selection scheme is applied iteratively. Here we present the initial applications on some benchmark systems indicate the capabilities of ASS1ST and the strengths and limitations are critically discussed.

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Ultrafast photodynamics simulations with *ab initio* multiple cloning approach

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We present the recent developments and applications of our *ab initio* multiple cloning (AIMC) method [1,2]. The idea of the method is to run non-adiabatic molecular dynamics on the fly using the basis of Gaussian coherent states moving along branching Ehrenfest trajectories thus combining some best features of Multiple Spawning [3] and Ehrenfest approaches [4].

We apply AIMC method to simulate processes of ultrafast photodynamics in a number of molecular systems. In particular, we have performed extensive simulations [5,6] of the photodissociation dynamics for various heterocyclic amines, such as pyrrole, imidazole, pyrazole, 2-ethylpyrrole, *etc* along with their selectively deuterated species. Our calculations reproduce well the main features of experimental TKER spectra and VMI images, as well as dissociation times and isotope effects, providing detailed insights into the experimental results.

Another area of our simulations is the intramolecular energy transfer in light-harvesting dendrimers. We have run AIMC simulations of the excitation dynamics for a set of different combinations of a chain of linked dendrimer building blocks [7]. The calculations show that the efficiency of the energy transfer strongly depends on the way how multiple chromophoric units have been assembled. The comparison between the results of AIMC and Ehrenfest dynamics demonstrates the importance of the wave function bifurcation in the case of larger dendrimers, which is accounted by the cloning procedure in the AIMC approach.

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Complexes of LPMO9c from *Neurospora crassa* with small-molecule inhibitors

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Lytic polysaccharide monooxygenases (LPMOs) are oxidative copper metalloenzymes with a key role in the conversion of complex biomass to fermentable sugars. Despite the high interest in sustainable production of biofuels and biochemicals, the enzymatic conversion of recalcitrant polysaccharides was falsely thought to be promoted only by hydrolases and LPMOs were discovered relatively recently [1]. LPMOs use hydrogen peroxide or oxygen as co-substrate binding to copper(I) in the active site. Oxidized LPMO possessing copper(II) has shown practically no activity, thus initial activation by a reducing agent, *e.g.* ascorbic acid is necessary [2]. After activation it appears to react through a Fenton-like mechanism similar to hexaaquacopper but some observations remain inconsistent and the exact mechanism is still debated [3]. Also works focused on inhibitors of LPMOs are scarce despite their importance. To shed more light into the field, we propose several small inhibitors of LPMO9c from *Neurospora crassa*. For certain species, a 50% drop of the activity was observed with millimolar inhibitor concentration (IC50). Similar results were observed for two different substrates. Considering competitive inhibition, we have calculated binding energies of inhibition complexes using DFT/B3LYP approach including the GD3BJ dispersion correction, PCM solvation model and the basis set superposition error estimation. We have found that inhibitors bind strongly to the active site and the binding energies correlate reasonably with the IC50 values supporting the experimental measurements. By separating the binding process into subprocesses of dehydration, deformation and interaction, we have quantified corresponding energies and their effect on the total binding affinity. The largest variance was observed for the interaction energies. Contributions of dehydration and deformation seem to improve inhibition prediction. Using the NBO analysis, the strongest stabilizing interactions were identified. Several off-site hydrogen bonds were found in complexes with strong binders. This work serves as one of the first LPMO inhibition studies, identifies several candidates for reversible LPMO inhibition and proposes a methodology for the prediction of their affinity.

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Acknowledgment

This work has been supported by Slovak Scientific Grant Agency VEGA (1/0416/17).

Relativistic 1s Core Orbital Shifts using Local Hybrid Functionals

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Relativistic effects play an important role in the accurate calculation of core properties, e.g. X-ray absorption spectra and core electron binding energies. Here, a common way to incorporate relativistic shifts of non-relativistic (NR) core-orbital energies is the a posteriori addition of atomic relativistic corrections, which, in many cases, are still determined using Hartree-Fock and a one-electron-relativistic Hamiltonian, i.e., two-electron relativistic effects and the dependence on the exchange-correlation (XC) functional, although being potentially significant, are fully neglected. In this work, the influence of the latter two factors on scalar-relativistic 1s core-orbital shifts has been investigated by employing the infinite-order two-component method[1] together with local hybrid functionals,[2,3] a recent class of hyper-generalized-gradient-approximation functionals, which, in contrast to most other XC functionals, is able to provide the correct high-density limit.

$$E_{xc}^{Lh} = E_x^{ex} + \sum_\sigma \int g_\sigma(\mathbf{r}) \cdot \left[e_{x,\sigma}^{ex}(\mathbf{r}) - e_{x,\sigma}^{sl}(\mathbf{r}) \right] \mathrm{d}\mathbf{r} + E_c^{sl} \tag{1}$$

First, we present the theoretical and technical details of our new scalar-relativistic implementation of local hybrid functionals in the RAQET program.[4] This includes the introduction of a picture-change transformation of the density matrix for an efficient treatment of relativistic two-electron contributions, an improved new screening procedure for the semi-numerical evaluation of exact-exchange integrals, and the derivation of a gauge correction that restores the correct iso-orbital limit of the relativistic kinetic energy density (KED). The effectiveness of these three approaches is illustrated for several representative cases. Furthermore, we provide accurate two-electron-relativistic 1s core-orbital energy shifts using several local hybrid functionals. Respective two-electron relativistic contributions and deviations of different XC functionals, in particular those differing just in the definition of the KED (NR and relativistic, with and without gauge correction) and the choice of the local exchange functional (NR and relativistic), are found to be in the order of magnitude of errors of XC functionals specialized for the calculation of core excitations. The mentioned factors are thus essential for a technically accurate calculation of relativistic core-orbital shifts and a sound comparison of different XC functionals.

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Composite Gaussian processes for probabilistic PES prediction

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The assignment of spectral lines in both the visible region and the UV region has important aplications in the study of astral objects such as stars and exoplanets, or, closer to us, in the study of the molecular composition of the terrestrial atmosphere. The correct assignment of spectra cannot rely solely on experimental results since those are not always available making theoretical predictions necessary.
To this end, we extended the use of Gaussian processes in PES prediction[1] to the use of composite machine learning Gaussian *regression* processes (c-GP) trained at different levels of theory, with different training sets, is explored. The final energy is a sum of composite probabilistic prediction corresponding to dense training sets at low levels of theory and sparse training sets on computationally expensive deterministic and stochastic[2,3] methods.
The study of the H_3^+ molecular ground singlet and triplet states and the performance of a prediction based on the HF surface with a correction based on the difference between the deterministic CCSD (equivalent to the FCI energy for H_3^+) energy and the HF energy is presented.
The prediction of both vibrational and rotational energy levels using the DVR3D[4] method is then applied to the obtained probabilistic PES for the ground singlet state.

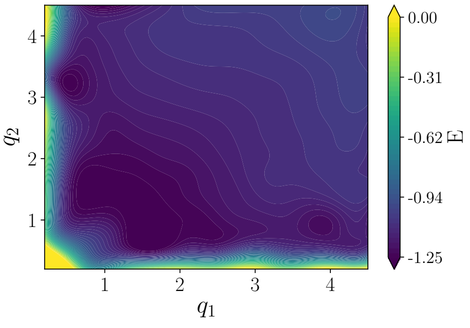

Figure 1: c-GP prediction for H_3^+

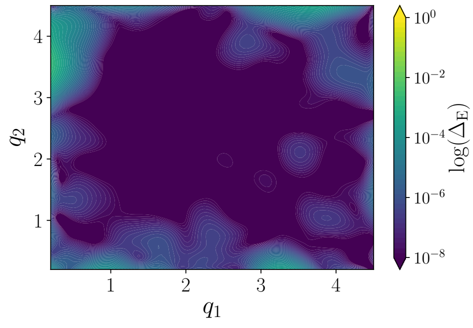

Figure 2: c-GP 95% confidence interval

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Recognition and Specificity in Base Excision Repair

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The Base excision repair (BER) system is a machinery of enzymes, recognising, removing, and correcting mispairs in the DNA. In the first step of the base excision repair system glycosylases recognise a damaged or mispaired base and remove it via glycosidic C1'-N1 bond hydrolysis. Apurinic/apyrimidinic endonuclease then cleaves the DNA backbone at the abasic site so as to allow subsequent insertion of a new, correct nucleotide by polymerase a and ultimately sealing of the backbone by a ligase enzyme. A crucial step in the base recognition and excision of mispared thymine (or damaged) bases by the BER enzyme human thymine DNA glycosylase (TDG) is the extrusion of the substrate base of the DNA helix and its "flip" into the active ste of the enzyme. The intrinsic conformational dynamics of mispaired DNA, exhibiting a partially-opened, partially flipped state [1], is exploited by the enzyme, stabilising this state over a closed state in the protein-DNA complex [2]. Further discrimination is achieved by the substrate base being better accommodated in the active site than non-cognate bases [2]. The glycosidic bond scission in the enzymatic complex is via a step-wise dissociative mechanism and largely facilitated by a proton transfer to the leaving base that is unlikely for intact cytosine bases. The chemical step can thus be understood as the last of several instances to protect intact DNA from base excision [3].

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Efficient Formulation of Full Configuration Interaction Quantum Monte Carlo in a Spin Eigenbasis via the Graphical Unitary Group Approach

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We provide a spin-adapted formulation of the Full Configuration Interaction Quantum Monte Carlo (FCIQMC) algorithm [1], based on the Graphical Unitary Group Approach (GUGA) [2], which enables the exploitation of SU(2) symmetry within this stochastic framework [3]. Random excitation generation and matrix element calculation on the Shavitt graph of GUGA can be efficiently implemented via a biasing procedure on the branching diagram.

The use of a spin-pure basis explicitly resolves the different spin-sectors and ensures that the stochastically sampled wavefunction is an eigenfunction of the total spin operator $\hat{\mathbf{S}}^2$. The method allows for the calculation of states with low or intermediate spin in systems dominated by Hund's first rule, which are otherwise generally inaccessible.
Furthermore, in systems with small spin gaps, the new methodology enables much more rapid convergence with respect to walker number and simulation time.

Some illustrative applications of the GUGA-FCIQMC method are provided: computation of the ${}^2F - {}^4F$ spin gap of the cobalt atom in large basis sets, achieving chemical accuracy to experiment, and the ${}^1\Sigma_g^+$, ${}^3\Sigma_g^+$, ${}^5\Sigma_g^+$, ${}^7\Sigma_g^+$ spin-gaps of the stretched N_2 molecule, an archetypal strongly correlated system.

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Redox-Mediated DNA Protection and Recognition of Defect Bases: Insights from Static QM Calculations and QM/MM Molecular Dynamics Simulations

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The ability of DNA to conduct charge has been documented extensively and it has been proposed that this ability can be employed by the cell for the recognition of DNA defects via charge transfer (CT) between base excision repair (BER) enzymes [1,2]. Exploiting differences in DNA redox chemistry introduced by the presence of a lesion, the defect is proposed to trap the migrating charge, thus disrupting DNA-mediated CT and initiating its repair process by base excision repair enzymes. For such a scheme, defect DNA fragments should have considerably different redox properties than their native counterparts.

8-oxoguanine (8OG), a product of guanine (G) oxidation, is the most abundant DNA lesion, and thus a highly relevant candidate for investigating this hypothesis. Recently, the ionization energies (IEs) and electron affinities (EAs) of native and 8OG-containing DNA models of up to 3 base pairs were determined by static DFT calculations under implicit solvation [3]. IEs were 0.2 eV lower for the defect fragments, while relative EA differences amounted to only 0.01 eV. Hole and excess electron distributions were consistent with these results (pronounced hole localization in 8OG, no differences for excess electron). In the context of a CT mechanism for the recognition of DNA damage, these findings strongly suggest that hole transfer is a more likely candidate than excess electron transfer. In fact, cyclic voltammetry experiments indicate that the detection of oxidative and bulky DNA lesions via hole transfer could be possible [4].

To gain more insight, it is essential to explicitly consider a biologically relevant environment (large DNA fragment, solvent, physiological ionic strength). Under this scope, we have performed QM/MM simulations of a native and a defect DNA 39mer in physiological conditions by means of hybrid DFT-based QM/MM simulations [5]. For the defect fragment, a G in a G-rich region was replaced by 8OG. Redox properties were determined using a theoretical method which is based on Warshel's theory on vertical energy gap distributions [6,7] and on Marcus Theory of electron transfer. The redox potential (E_{ox}) of 8OG-DNA is approximately 1 eV higher than that of its native counterpart. This outcome highlights 8OG's oxidizing power, and supports a potential DNA-mediated hole transfer scheme for the recognition of oxidative DNA lesions. In order to assess whether such a finding also applies to other DNA sequences and lesions, we are currently simulating the oxidation of an adenine (A)-rich region of the same DNA 39mer at the QM/MM level. In the defect fragment, one A is replaced by an isoguanine (IG) defect.

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Divide-and-conquer DFTB-MD simulations of polaron formation process in a lead halide perovskite material

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In solids, negative or positive charge carriers wear the strutural deformation and form polarons. Polarons play key role in photo-electronic devices, for instance, solar cells. In perovskite solar cells, which are photovoltaic devices constructed by lead halide perovskites (LHPs), extremely long lifetime and diffusion length of charge carriers is observed. In order to elucidate the mechanism underlying these properties, polaron formation mechanism in LHPs needs to be clarified. In particular, there is an open discussion over the role of rotational motion of the organic molecular cations ($CH_3NH_3^+ = MA^+$) incorporated in the LHPs, which might protect the charge carriers from electron–hole recombination. While quantum mechanical (QM) molecular dynamics (MD) is a promising way to unvail the polaron formation process, the spatial size of the polarons, which is estimated at nm scale, is not accessible by conventional first-principles MD technique such as Kohn–Sham density functional theory because of their computational cost. In this work, we employed the divide-and-conquer type density-functional tight-binding (DC-DFTB)[1,2], which is a linear scaling semiempirical quantum chemical calculation method capable of picoseconds MD simulations for systems composed of thousands of atoms. We tracked the polaron formation process in $MAPbI_3$, which is a representative LHP material, by DC-DFTB-MD simulations with the use of a 3.7 nm × 3.7 nm × 5.4 nm simulation cell (3,072 atoms) to obtain a realistic description of the polaron. The calculations were conducted with DCDFTBMD code[2]. Snapshots of spatial distibutions of the charge carriers are depicted in Figure 1. We found the structural dynamics of not only the MA^+ but also the remaining part of the material, PbI_3^-, involve the polaron formation. Also, we established that the polaron formation occurs in two distinct steps; the charge localization attributed to the thermal fluctuation of the structure, and the further structural deformation induced by the charge carrier. In addition, in order to provide a hint for the abovementioned hypothesis, that is, importance of the MA^+, we evaluated the energetical contribution of the PbI_3^- framework and the MA^+. Further details will be presented in the poster.

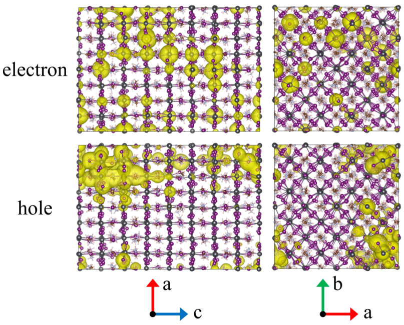

Figure 1: Snapshots of spatial distribution of negative (upper) and positive (lower) charge carriers.

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Excited-state coupled-cluster frozen-density embedding for large systems

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Supermolecular calculations for systems containing an increased number of molecules suffer from two main drawbacks. These are, first, the non-linear and often steep scaling with system size and, second, a complex analysis due to delocalized orbitals or response vectors. These two drawbacks can be circumvented using frozen-density embedding (FDE) [1], which partitions the supersystem into the individual molecules and has been found to be a versatile tool to study molecules in complex environments.

Combining FDE with coupled-cluster methods can be achieved in a rigorous manner when using the Lagrangian approach, enabling an efficient treatment of excited-state response properties such as orbital-relaxed dipole moments and analytical gradients for coupled-cluster methods embedded in a density-functional theory (DFT) environment. Finally, the accuracy and efficiency is illustrated using biological model systems containing about 30 molecules consisting of about 360 atoms in total, for which orbital-relaxed excited-state properties can be computed on standard compute nodes using coupled cluster FDE [2,3].

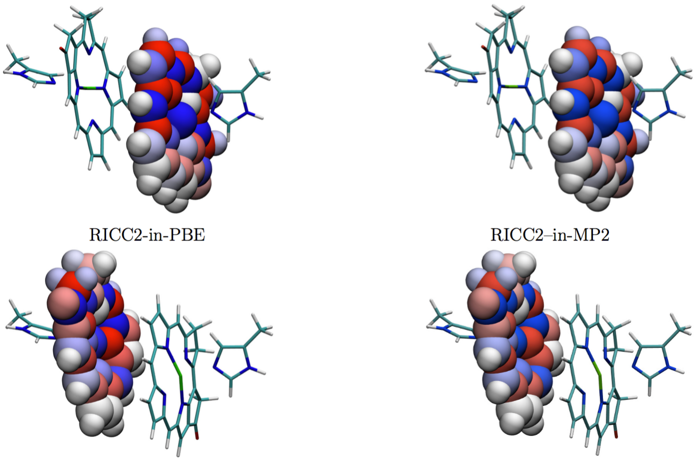

Figure 1: Orbital-relaxed excited-state atomic charges computed using FDE.

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Rates of Proton Transfer in Water from Semi-Empirical QM/MM Simulations

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The long-term goal of our research is the development of novel magnetic resonance imaging (MRI) methodologies for the characterization of musculoskeletal tissues (in particular articular cartilage). Currently, we are focussing on strategies based on the longitudinal relaxation time in the rotating frame ($T_{1\rho}$). One of the mechanisms most likely contributing to the dispersion of $T_{1\rho}$ in many tissue types is the chemical exchange of protons between biomacromolecules and water. Due to the system size required to model representative fragments of the biomacromolecules with a significant water shell over a time frame long enough to characterise the proton transfer processes in question, we expect only quantum chemical methods with the very low resource requirements to be applicable to the problem. Therefore, we present here an overview over the performance of a series of semi-empirical methods with regards to the description of proton transfer processes in water.

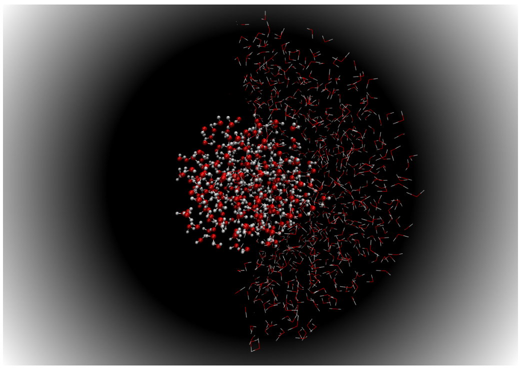

Figure 1: Schematic QM/MM system setup for excess hydrated proton simulations.

The system setup we have used for our simulations is illustrated in Figure 1: an $r = 12$ Å sphere of water molecules containing one excess proton is surrounded by a shell of classically simulated water molecules with a thickness of 10 Å. For each of the semi-empirical model chemistries 10 trajectories with a total length of 0.5 ns were run. Most of the methods tested were able to give proton transfer rate within an order of magnitude of the experimental value. Results from these calculation, combined with stationary calculations of the proton affinities of chondroitin sulfate, suggest escpecially PM7 and DFTB3-D3 as promising candidates for ensuing simulations including biomolecular fragments.

Density functional correlation theories based on the Unsöld approximation

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We present Unsöld-W12 (UW12) an approximate method for including explicit correlation in density functional theory [1, 2]. The approximation has a similar form to second-order Møller–Plesset (MP2) theory, without the dependence on virtual orbitals. Therefore, unlike double hybrid functionals, the approximation does not suffer from poor basis set convergence and is fully self-consistent.
We showcase two exchange—correlation functionals based on this approach; XCH-BLYP-UW12 and fB-LYP-osUW12, demonstrating their performance for small systems. These functionals, among other advantages contain an exceptionally small amount of self-interaction error; the cause of many problems in density functional theory.
We also consider possible new functional forms for the approximation.

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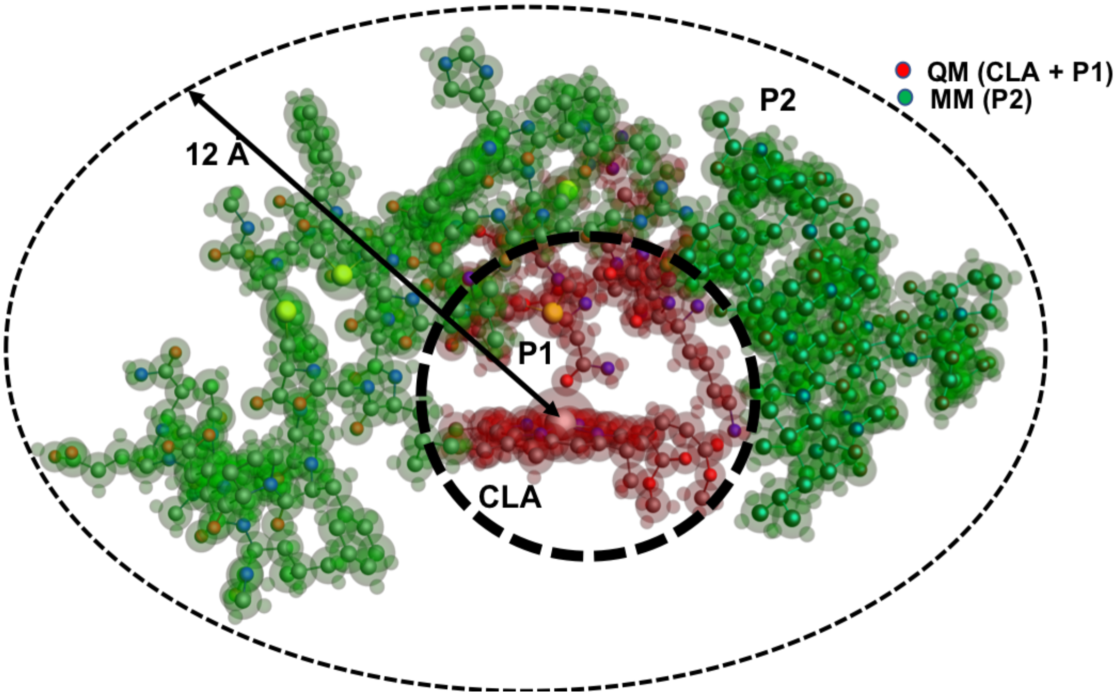
Light Harvesting Complex II (LHCII) is on of the major pigment complex in higher plants largely responsible for light absorption and energy transfer. Studies have shown that LHCII can switch its functionality between a photo-active and a photo-quenched state, manifested by a change in the conformation and excitonic interaction between the chlorophyll and carotenoids. In order to study the effect of the protein environment on the absorption energy of chlorophyll, we focused on a putative quenching site as proposed previously and establish an optimum full protein model which could be treated accurately and at the same time describing the electrostatics involved in protein dynamics. Starting with the crystal structure we selected an environment of 12 Å around the Mg center of a chlorophyll a (denoted herby as CLA612) at the quenching site and modelled it using different QM and QM/MM techniques. We divided the environment depending on the proximity of the residues to the chlorophyll. We treated the nearby residues in an accurate QM way and the far away residues in a more approximate way using point charges and polarizabilities under the Discrete Reaction Field (DRF) model. On comparing our results, we concluded that the far away residues do not have any direct and significant effect upon the absorption energy as long as we do not distort the crystal structure and produce artefacts in the structure.



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Quantum Dynamical Effects on ^{3}He NMR in Endohedral Fullerenes

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The presence of a cavity inside fullerenes allows the introduction of guest atoms or small molecules inside the cage, *e.g.*, noble gas atoms such as ^{3}He [1], forming the so-called endohedral fullerenes. Experimentally observed ^{3}He NMR shift differences for fullerenes with one and two helium atoms [2] are here treated with path-integral Monte Carlo (PIMC) simulations of He and He_2 in neutral C_{60} and C_{70}, as well as their hexa-anions [3]. The potential energy (PES) and ^{3}He chemical shift surfaces are modelled at first-principles SCS-MP2 and DFT levels, respectively. The method provides information about the quantum dynamical effects of both helium and carbon atoms on ^{3}He NMR shifts at different temperatures.

With the efficient PIMC implementation, these pre-parametrised energy and NMR property surfaces also enable the study of *negative* thermal expansion (thermal contraction) of the C_{60} fullerene [3]. We can show that the effect is clearly observable in the ^{3}He NMR shift and we propose endohedral noble gas NMR as a complementary method to investigate the thermal expansion of fullerenes and other nanostructures with cavities in addition to Raman and infrared spectroscopies as well as noble gas EXAFS [4,5].

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EFFECT OF SOLVATION ON KINETIC ISOTOPE EFFECTS ON HYDROGEN ABSTRACTION FROM ETHANOL IN AQUEOUS SOLUTION

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Hydrogen abstraction from ethanol by atomic hydrogen is a well-known reaction which is one of the most important steps in ethanol decomposition.[1] Depending on the temperature this reaction can proceed via three different channels resulting in three different products. It has been shown that at room temperature this reaction goes through only one pathway, however, the reaction can proceed via two transition states (gauche (g) and trans (t)) which interconvert in each other by internal rotation.[2,3] Previous computational study on this reaction was focused on using the simplest presentation of solvent - continuum model of solvation and it was observed that the resulted hydrogen kinetic isotope effects (^{2}H KIEs) deviate from the experimental data which may appear due to the lack of inclusion of specific interactions with the environment. Current research efforts focus on expanding the solvation model in order to test the effect of the explicit presence of water molecules on predicted isotope effects.

^{2}H KIEs were calculated for four different substitution scenarios using two theoretical approaches; multi-path variational transition state theory (MP-VTST) [3,4] and a path integral formalism in a combination with free-energy perturbation and umbrella sampling (PI-FEP/UM).[5] The former method allowed for incorporating quantum effects such as tunneling and recrossing for multiple reaction paths with thermal rate constants determination which were further used for kinetic isotope effects calculation. The latter method enabled to treat the solvent purely explicitly by using a QM/MM protocol. It was observed that within the MP-VTST approach inclusion of a small number of water molecules did not always improve the predictions and the path integral model succeeded only when the QM region of the model was treated at a DFT level of theory. The influence of environment on the obtained isotopic fractionation as well as the contribution of various factors like conformation of the transition state and the position of water molecules directly interacting with the solute were analyzed and discussed.

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Theoretical Insights to Novel Beryllium Reactivity

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Recent reports have found beryllium to facilitate the activation of relatively inert chemical bonds. Therefore, interest in beryllium chemistry has grown significantly in recent years with a number of beryllium compounds stabilised by N-heterocyclic carbene (NHCs) and cyclic (alkyl) (amino) carbene (CAACs). We report results of theoretical investigations for a series of novel beryllium carbodicarbenes (CDC) in collaboration with synthetic studies.[1-3] We have utilized Atoms in Molecules (AIM) calculations and Energy Decomposition Analysis (EDA) to determine the local electronic environment of **1** and **2**. Further we have undertaken mechanistic studies to understand different reactivity to form **3** and **4**.[4]

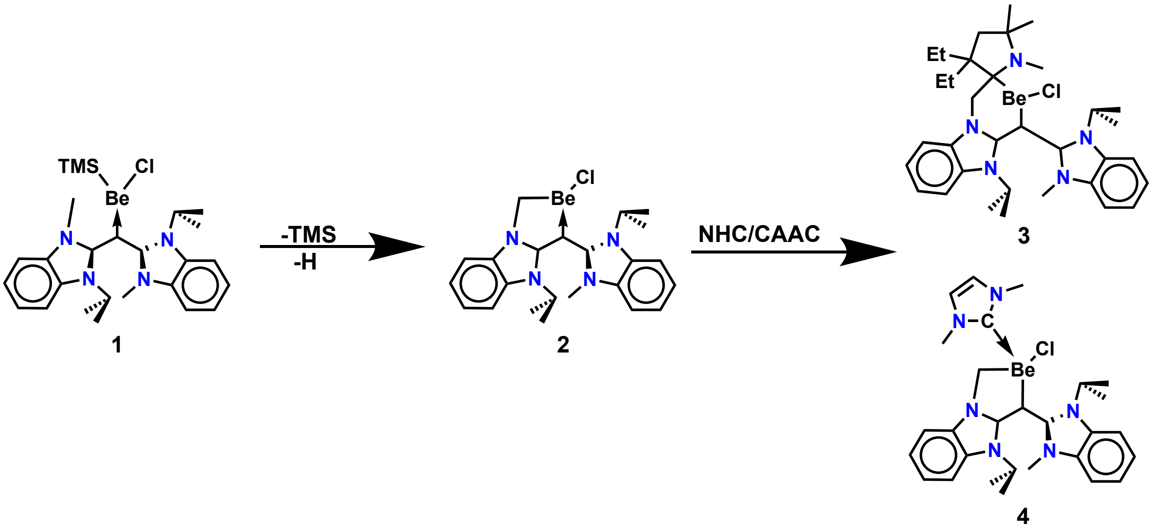

Figure 1: CAAC-promoted ring expansion of beryllium.

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Search for Optimal Arrangements of Perylene Pairs in Singlet Fission

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A multiple exciton generation, such as singlet fission (SF), in which one singlet exciton splits into two triplets could be utilized in organic photovoltaic materials to surpass the Schockley-Queisser limit.[1] The rate of SF depends not only on the excited states of the molecules but also their packing arrangements. Time-resolved spectroscopy has been carried out to investigate the SF rate for the crystal packing of perylene diimide (PDI).[2] Understanding the relationship between the packing arrangements and SF process plays an important role in tuning the favorable molecular pairs. A simple model described by the diabatic frontier orbitals is applied in searching for the local maximum rate of SF.[3] First, we examine the value of the square of the electronic matrix element in six-dimensional space. Then, the SF rates in the local maxima of molecular pairs were obtained with the approximation of the Marcus theory. A few molecular pairs of PDI and terylene diimide (TDI) have been found with fast SF rates to compare with their parental pairs in this simple model. These optimized geometries would provide a guideline for crystal engineering or covalent dimer synthesis in SF materials.

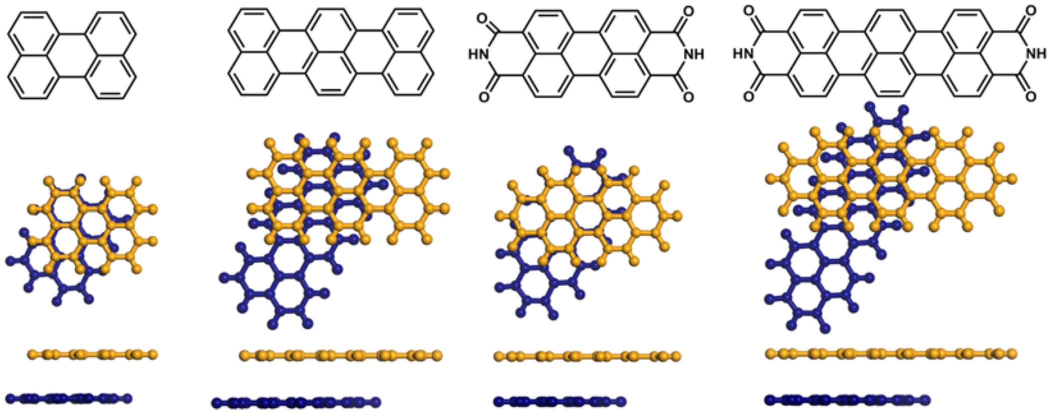

Figure 1: Optimal arrangements of molecular pairs for singlet fission.

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Exploring the Combination of Linear Response and State Specific Approaches for a More Accurate Description of Excited States in Solution

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Time-Dependent Density Functional Theory (TD-DFT) has emerged as the method affording the best compromise between accuracy and computational cost, for the study of molecular excited states [1]. For the same reason, the Polarizable Continuum Model (PCM) [2] has become the preferred approach for the description of solvent effects on the structure and the electronic properties of molecular solutes. The combination of TD-DFT and PCM with the goal of providing an accurate picture of excited states in solution is – however – less than straightforward. One of two approaches is usually chosen: in the linear-response approach solvation effects arise from the electric transition dipole, while in the state-specific approach the change in the molecular dipole associated with the electronic transition modifies the self-consistent reaction field established for the ground state. In addition, while both approaches can be used to describe non-equilibrium solvent effects on absorption, only the state-specific one provides a consistent description of a non-equilibrium emission process. By itself, each one of the linear-response or the state-specific approach provides a partial picture of the actual physical phenomenon. The solvent effect on a very bright transition not associated with a significant change in the molecular electric dipole is unlikely to be well described by the state-specific approach. On the other hand, the linear-response approach seems ill-suited to describe the solvent effect on a dark transition which nevertheless involves a redistribution of charge. In this contribution, we present a compact implementation of a method that combines the two approaches in an effective and useful way. The usual linear-response approach and the state-specific Vertical Excitation Model (VEM) [3] are combined with user-defined weights, with the goal of providing the best description of each electronic transition based on its characteristics. Moreover, if the orbital relaxation terms are excluded from the VEM, the analytic gradient of the combined approach is readily available [4,5], allowing for the study of the excited state potential energy.

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Iron Doped Gold Cluster Nanomagnets: *Ab Initio* Determination of Barriers for Demagnetization

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Magnetic properties of small- and nano-sized iron doped gold clusters are calculated at the level of second order multireference perturbation theory. We first assess the methodology for small Au_6Fe and Au_7Fe clusters, which are representative of even and odd electron count systems. We find that larger active spaces are needed for the odd electron count system, Au_7Fe, which exhibits isotropic magnetization behaviour. On the other hand, the even electron count system, Au_6Fe, exhibits strong axial magnetic anisotropy. We then apply this methodology to the tetrahedral and truncated pyramidal nano-sized $Au_{19}Fe$ (with S=3/2) and $Au_{18}Fe$ (with S=2) clusters. We find that face substitutions result in the most stable structures, followed by edge and corner substitutions. However, for $Au_{18}Fe$, corner substitution results in strong magnetic anisotropy and a large barrier for demagnetization while face substitution does not. Thus, although corner and face substituted $Au_{18}Fe$ have the same spin, only corner substituted $Au_{18}Fe$ can act as a single nanoparticle magnet.

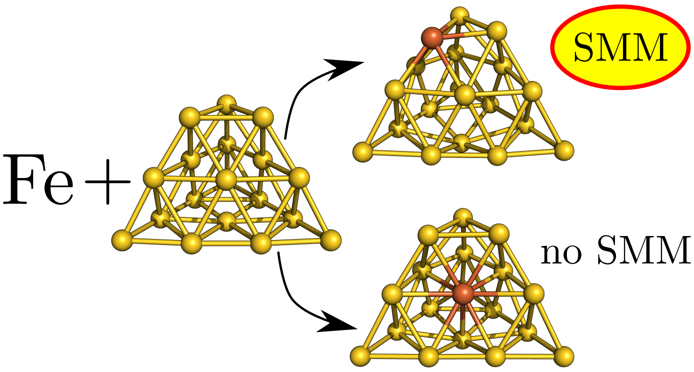

Figure 1: Single molecule magnet properties depend on the substitution scheme.

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Which quantum statistics–classical dynamics method is best for water?

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There are a variety of methods for including nuclear quantum effects in dynamics simulations by combining quantum Boltzmann statistics with classical dynamics. Among them are thermostatted ring-polymer molecular dynamics (TRPMD) [1], centroid molecular dynamics (CMD) [2], quasi-centroid molecular dynamics (QCMD) [3], and the linearised semi-classical initial value representation (LSC-IVR) [4]. Here we make a systematic comparison of these methods by calculating the infrared spectrum of water in the gas phase, and in the liquid and ice phases (using the q-TIP4P/F model potential [5]). Some of these results are taken from previous work, some of them are new (including the LSC-IVR calculations for ice, and extensions of all the spectra into the near-infrared region dominated by overtone and combination bands). Our results suggest that QCMD is the best method for reproducing fundamental transitions in the spectrum, and that LSC-IVR gives the best overall description of the spectrum (albeit with large errors in the bend fundamental band caused by zero-point-energy leakage). The TRPMD method gives damped spectra that line up with the QCMD spectra, and is by far the cheapest method [6].

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Inclusion of Machine Learning Kernel Ridge Regression Potential Energy Surfaces in On-the-Fly Nonadiabatic Molecular Dynamics Simulation

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We discuss a theoretical approach that employs machine learning potential energy surfaces (ML-PESs) in the nonadiabatic dynamics simulation of polyatomic systems by taking 6-aminopyrimidine as a typical example. The Zhu-Nakamura theory is employed in the surface hopping dynamics, which does not require the calculation of the nonadiabatic coupling vectors. The kernel ridge regression is used in the construction of the adiabatic PESs. In the nonadiabatic dynamics simulation, we use ML-PESs for most geometries and switch back to the electronic structure calculations for a few geometries either near the S_1/S_0 conical intersections or in the out-of-confidence regions. The dynamics results based on ML-PESs are consistent with those based on CASSCF PESs. The ML-PESs are further used to achieve the highly efficient massive dynamics simulations with a large number of trajectories. This work displays the powerful role of ML methods in the nonadiabatic dynamics simulation of polyatomic systems.

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Linearization of Moment Tensor Potentials

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Moment Tensor Potentials (MTP) are a method of approximation of molecular potential energy surfaces, with application in machine learning models [1]. In the published formulation, the model is non-linear and requires nonlinear optimization techniques for parametrization.

We propose an alternative relaxed formulation of the original potential energy function where parameter optimization is expressed as a linear sparse approximation problem. This change leads to very large number of highly multi-collinear variables (e.g. 49156 for the water dimer) which brings about the need to introduce heuristic approaches to reduce the set. We used importance ranking of variables and Bayesian information criterion to reduce the number of variables by more than an order of magnitude (e.g. to 4200 for the water dimer).

The proposed formulation was tested on water dimer and water trimer with MTP expansion including up to 4-body terms, with the training set comprising approximately 38000 configurations for water dimer and 11000 configurations for water trimer and their corresponding energies obtained from CCSD(T) calculations extrapolated to basis set limit.

The models provide approximations to the short-range quantum-mechanical supplement of a classical polarizable potential [2] with a RMSE of 0.0393 kcal/mol for the water dimer for a test set of 4235 data points not used in the fitting. For the water trimer, the corresponding figures are 0.1179 kcal/mol and 1235 points in the test set.

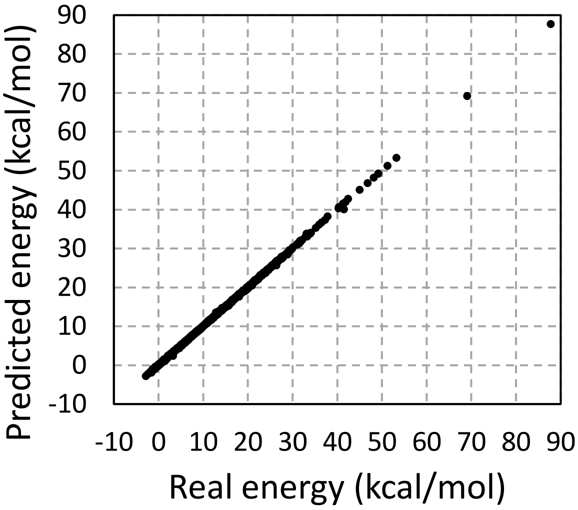

Figure 1: Parity chart for comparing the actual 3B interaction energy values of the test set with those obtained from the model.

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This work was supported by Estonian Research Council grant PUT1683.

Strong light-molecule coupling can enhance the photoisomerization quantum yield.

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The control of photochemical reactions calls for the selective enhancement and quenching of individual processes among those occurring when light, molecules and environment interact. To this aim, the strong coupling between molecules and cavities offers a toolbox of new effects to control the photochemical reactions[1]. In this regime, the molecular degrees of freedom mix with the resonant cavity photons[2], yielding hybrid light-matter states: polaritons.

In this work, we resort to a FOMO-CI[3] based approach to investigate the influence of the strong coupling on the azobenzene excited state taking into account all the molecular complexity. Traditionally, the study of photochemical processes relies on a compromise between efficiency and accuracy. In this regards, non-adiabatic dynamics techniques in the semiclassical framework have been developed (Surface hopping algorithms)[4]. By reworking one of such techniques, we take into account the hybrid light-matter nature of polaritonic states and investigate the photochemistry on polaritonic states of azobenzene in vacuum[5]. Basing our QM/MM simulations on a recent experimental realisation[6], we present the results of the photochemistry for a realistic system under the strong coupling regime. We describe how such coupling deeply affects the quantum yields of a photoisomerization process and its mechanism, discussing how suitable conditions can be found to selectively suppress or enhance reaction quantum yields. Finally, we comment on the impact of such modified photochemistry on the control of the concentration of product at the photostationary state.

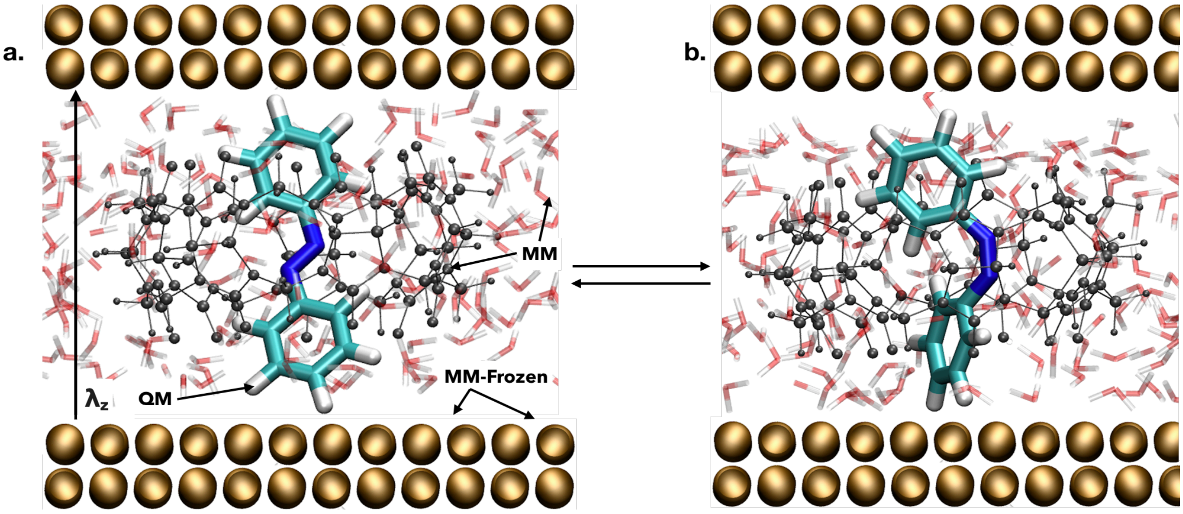

Figure 1: Simulated azobenzene photoreversible switch between trans(a) and cis(b) under strong coupling regime. The system mimics the experimental realization of ref.[6] by treating azobenzene at QM level. The environment is modeled by electrostatic embedding plus Lennard-Jones potentials.

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Accuracy of Excited State Spin-Component-Scaled CC2 potential energy surfaces

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Benchmark calculations with the Spin-Component-Scaled CC2 variants SCS-CC2[1,2] and SOS-CC2[3] are presented for the electronically excited valence and Rydberg states of small and medium-sized molecules. Besides the vertical excitation energies and excited state gradients, the potential energy surfaces are also investigated via scans following the forces that act in the Franck-Condon region. The results are compared to higher level methods CCSD, CCSD(T)(a)* and CCSDT, as well as to the regular CC2. For the latter, serious flaws have been revealed by an earlier study.[4] The results indicate that a large fraction of these flaws disappear if spin-component-scaling is employed, making these variants attractive alternatives of CC2, offering competitive accuracy of vertical excitation energies of both valence and Rydberg type states, reliable potential energy surfaces, while also maintaining a low-power scaling computational cost with the system size.

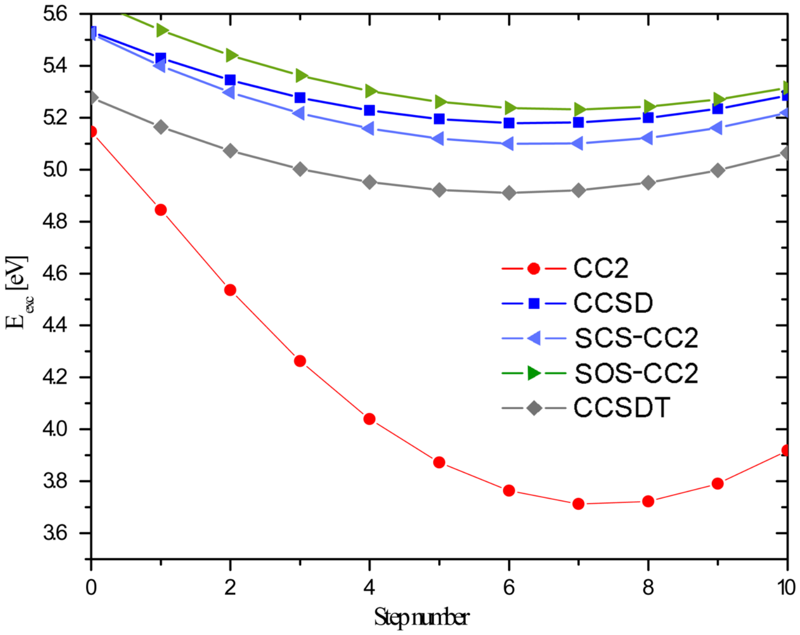

Figure 1: : Illustrative potential energy surface scan for cytosine.

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Dissociative electron attachment to SF_5CF_3 leading to a stable combination of anionic SF_4 and neutral CF_4: Ab initio molecular dynamics study

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Since the first claim of its potential global warming effect of SF_5CF_3, almost two decades ago,[1] numerous experimental and theoretical studies were carried out to provide deeper understanding about its fate in the earth's atmosphere, as reviewed in a book chapter.[2] Among all possible removal processes of SF_5CF_3 from atmospheric environment, its reaction with low-energy electrons in the mesosphere is regarded to be the most probable pathway. Several research groups have made related experimental and theoretical studies,[3-6] and confirmed the production of the anionic product (SF_5^-) and radical (CF_3). So far, the fragment anion, SF_5^-, is assumed not recycled by its subsequent reaction with other chemical species. The energetic property of the product combination, neither the combination of anionic product (SF_5^-) and radical (CF_3) nor their dipole bound complex anion,[5] however, is not stable enough to be considered as an ultimately stable stage of the dissociative electron attachment. According to our theoretical study, as shown in this work,[7] there exists an additional pathway leading to the more stable combination of anionic SF_4 and neutral CF_4 by the recombination of the initial fragments, the anionic product (SF_5^-) and radical (CF_3), produced in the first stage of the electron attachment to SF_5CF_3. Ab initio calculations and subsequent classical molecular dynamics studies were carried out in the present work to support our new claim.

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Computational modelling of the ionization of organic biradicals

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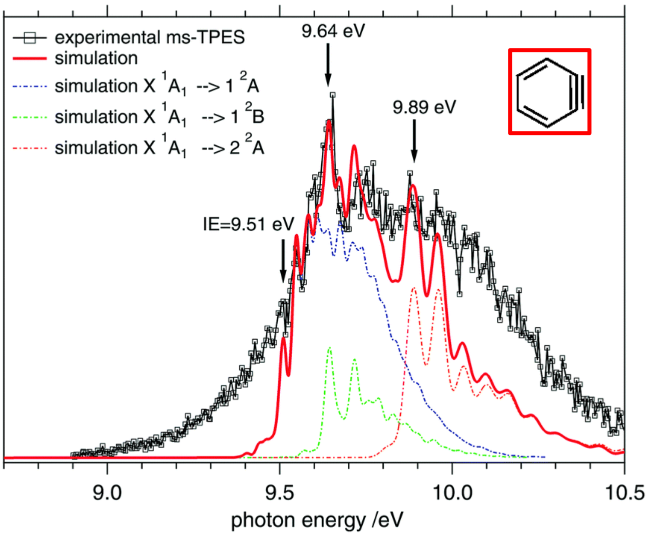
We use high-level computational approaches to investigate the spectroscopy of the organic biradicals *ortho*-benzyne and pentadiynylidene. Comparison with experimental data obtained from mass-selective threshold photoelectron spectroscopy highlights the varying goodness of different quantum-chemical approaches. For both systems, more approximative methods can be seen to fail even in the qualitatively correct prediction of the system's structure & properties. We highlight these potential pitfalls and conclude some key learning for the accurate prediction of ionization energies of biradicals.



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Theoretical investigation of effect of alkylation and bromination on spin-orbit couplings in BODIPY based photosensitizers

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Halogenated and alkylated BODIPY derivatives are emerging as important photosensitizers for their use in photodynamic therapy of cancer cells due to their high triplet quantum yield [1]. Spin-orbit couplings (SOCs) inducing intersystem crossing in these molecules is evaluated with an effective one-electron spin–orbit Hamiltonian. Matrix elements of an effective one-electron spin–orbit Hamiltonian between singlet and triplet configuration interaction singles (CIS) auxiliary wave functions are calculated using a new code capable of dealing with singlets and both restricted and unrestricted triplets built up from up to three different and independent sets of (singlet, alpha and beta) molecular orbitals [2].

BODIPY's with halogen atoms are found to have SOCs significantly greater than BODIPY's possessing just alkyl moieties. Excited state dynamics of brominated-BODIPY was further explored with TD-DFT surface hopping molecular dynamics on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit (SO) coupling. For the surface hopping trajectories, an accelerated MD approach was used, in which the SO couplings are scaled up, to make the calculations computationally feasible and the life times are extrapolated back to unscaled SO couplings. The life time of the first excited singlet state estimated by semi-classical surface hopping simulations is 180±75 ps [3].

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Is it possible to predict supercritical properties by *ab initio* molecular dynamics simulation?: Effective Fragment Potential version 2 - Molecular Dynamics (EFP2-MD) simulation study

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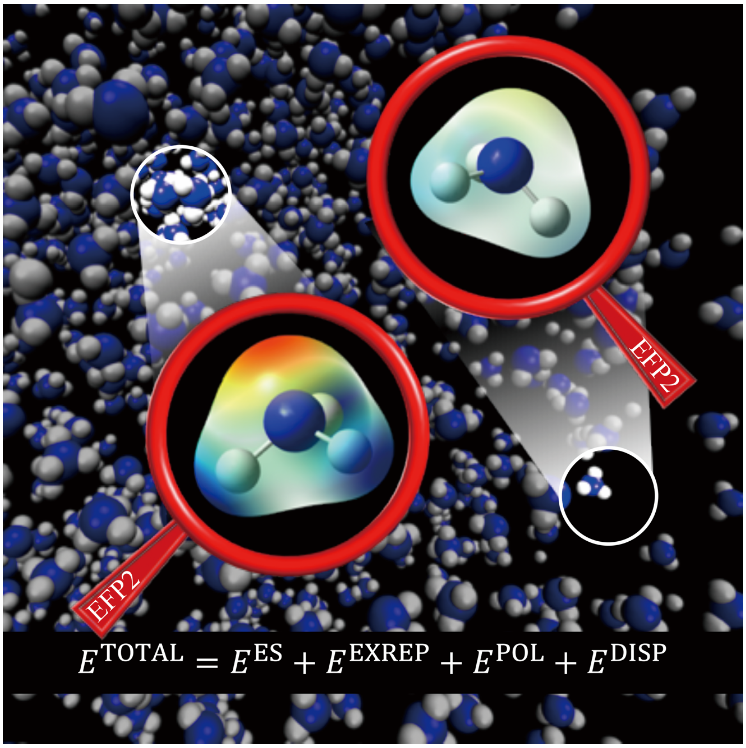
Effective fragment potential version 2-molecular dynamics (EFP2-MD) simulations, where the EFP2 is a polarizable force field based on ab initio electronic structure calculations, were applied to predict the static and dynamic liquid properties of compressed liquid NH_3. By analyzing the temperature dependence of the radial distribution function, the autocorrelation functions of velocity ($C_v(t)$) and reorientation ($C_r(t)$), and the self-diffusion constant, we clarified that the ab initio EFP2 force field can effectively describe the properties of compressed liquids. These descriptions can be performed with at least semiquantitative accuracy and at a sufficiently low computational cost. In the EFP2-MD protocol, no force field training is required. This training is mandatory when simulating liquid properties with classical MD techniques (especially in extreme conditions with high pressures and temperatures). EFP2-MD is a promising technique for predicting the physicochemical properties of novel functional compressed liquids, including supercritical fluid phase properties.



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Molecular Vibrational Frequencies and the Diagonal Born-Oppenheimer Correction within the Nuclear-Electronic Orbital Framework

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Multicomponent quantum chemical methods, where more than one type of particle is treated quantum mechanically, are employed to investigate nuclear quantum effects. The nuclear-electronic orbital (NEO) method treats select nuclei, typically protons, quantum mechanically on the same level as the electrons [1]. A variety of multicomponent density functional theory and wavefunction based methods have been developed within the NEO framework.

A challenge within the NEO framework is the calculation of molecular vibrational frequencies that include motions of both classical and quantum nuclei for comparison to experimental spectra. To compute such vibrational frequencies, an extended NEO Hessian that depends on the expectation values of the quantum nuclei as well as the coordinates of the classical nuclei is constructed and diagonalized [2]. This extended Hessian is constructed from quantities related to vibrational excitations calculated with multicomponent time-dependent density functional theory. The resulting vibrational frequencies for a series of molecular systems, including those with multiple quantum protons, demonstrate that this method includes the significant anharmonicity in the quantum proton stretching modes.

Another issue that arises within the NEO framework is the validity of the Born-Oppenheimer separation between the quantum protons and the other nuclei. The diagonal Born-Oppenheimer correction (DBOC) in the NEO framework has been derived and applied to a series of molecular systems. The effect of including the DBOC in the NEO potential energy surface for a series of molecules has been found to be negligible, with equilibrium geometries changing on the order of 10^{-4} Å and heavy atom stretching frequencies changing by ~1–2 cm^{-1} per quantum proton that is bonded to a heavy nucleus participating in the vibrational mode. These results suggest that inclusion of the DBOC does not significantly impact the potential energy surface.

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Funnel metadynamics on the Kelch domain of Keap1.

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Funnel metadynamics is a method that allows a ligand to enhance the sampling of the target binding sites and its solvated states. In this method, a funnel-shaped potential is applied to the system, reducing the space to explore in the unbound state. During the simulation, the system visits the bound and unbound states several times, allowing an accurate estimation of the binding free-energy surface within a reasonable simulation time [1]. In this work, we performed funnel metadynamics on a DLGex peptide and the Kelch domain of Keap1. The peptide contains the "DLG" motif necessary in Neh2 for Kelch binding. The Neh2 domain is an important transcription factor responsible for the cell's defense against oxidative stress. The initial structure for the peptide was taken from a 1 μs trajectory with the Amber99SB*-ILDNP force field, and the Kelch domain was retrieved from the Protein Data Bank.

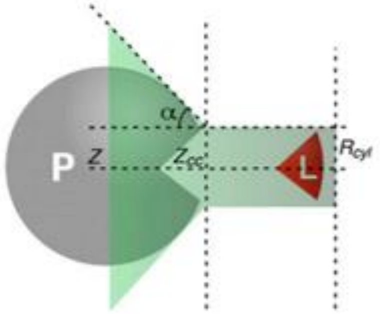

Figure 1: Schematic representation of the funnel restraint potential used in FM calculations. The shape of the funnel can be customized on the target by setting a few parameters. Given z, the axis defining the binding path of the ligand, z_{cc} is the distance at which the potential changes from a cone shape into a cylinder. The α angle defines the amplitude of the cone and R_{cyl} is the radius of the cylindrical section [1].

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$|\Psi|^2$ Analysis: Electronic Motifs and Energy Partitioning with Quantum Monte Carlo

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Local properties of a chemical system are contained in its many-electron wave function Ψ but extraction of information about bonding and stability is increasingly difficult for growing electron numbers N because of the high dimensionality.
Often, orbital localization or electron density methods are employed for which correlation is lost in the three-dimensional data. Alternatively, valence bond theory can be used and provides insight into local properties such as structure weights and resonance energies but is limited to a specific wave function ansatz.

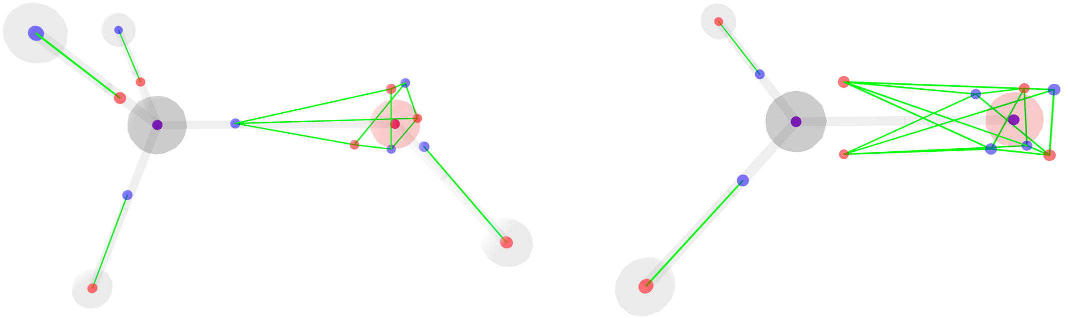

Figure: Electronic motifs in probable maxima of methanol (left) and formaldehyde (right). Blue and red spheres represent α and β electrons and green lines indicate opposite-spin correlation between them.

We present a different, quantum Monte Carlo-based approach relying on importance sampling of the $3N$-dimensional probability density $|\Psi|^2$ and remaining flexible in the wave function ansatz[1]. Subsequent local maximization of the sample yields maxima providing a natural partitioning of $|\Psi|^2$ into $3N$-dimensional basins of attraction. The maxima can then be clustered based on their similarity. In the resulting clusters, we find transferable and recurrent motifs of spin-correlated electron positions (see Figure) clearly showing the interplay of Coulomb interaction and Pauli repulsion[1].
The local energy contributions obtained during the quantum Monte Carlo sampling allow for assigning intrinsic interaction energies to the motifs of the individual clusters.
In this work, we present the latest $|\Psi|^2$ analysis results for common organic molecules.

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Atomic and electronic structure analysis of Pd@Ag core-shell nanoparticles by large-scale DFT calculations

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Large-scale density functional theory (DFT) can play an important role to clarify the active sites of catalytic reactions in metallic nanoparticle systems by investigating the site- and size-dependence of atomic and electronic structures and reaction properties. Our large-scale DFT code CONQUEST [1] can treat large systems containing more than several thousands of atoms by using local orbitals and a linear-scaling ($O(N)$) method. CONQUEST achieves $O(N)$ by using the locality of density matrices with the density matrix minimization method. Local orbitals, which are called support functions, are used to express the density matrices.

The computational cost scales cubically to the number of the support functions, both in the $O(N)$ and the conventional diagonalization calculations. Therefore, to reduce the number of support functions without losing accuracy, we have introduced multi-site support functions (MSSF) [2,3]. MSSFs are the linear combinations of pseudo-atomic orbitals from a target atom and its neighbor atoms in a cutoff region.

$$\phi_{I\alpha}(r) = \sum_{K}^{neighbours} \sum_{\mu \in K} C_{I\alpha,K\mu} \chi_{K\mu}(r)$$

MSSFs correspond to local molecular orbitals so that the number of required support functions can be the minimal. While the $O(N)$ method is not guaranteed to be applicable for metallic systems, the multi-site method can be applied for metallic systems stably.

In this study, we have investigated the selective semihydrogenation of alkynes with core-Pd/shell-Ag (Pd@Ag) nanoparticles by using the multi-site method. Pd@Ag accelerates the hydrogenation from alkyne to alkene but prevent the overhydrogenation from alkene to alkane [4]. To clarify the catalytic mechanism of Pd@Ag, we investigated the atomic and electronic structures of Pd, Ag and Pd@Ag nanoparticles. It is found that the surfaces of Ag nanoparticles are charged negatively, while that of the Pd nanoparticle is partially charged negatively. We will also report the electronic structure dependence of Pd@Ag on the Ag-shell thickness and the effect from the Pd/Ag interface to the particle surface.

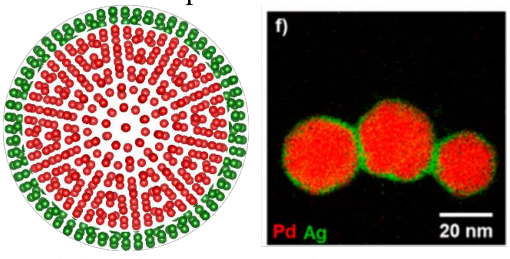

Figure 1: Simulation model and experimental image [4] of Pd@Ag nanoparticles.

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Theoretical Challenges of Enantioselectivity in Asymmetric Hydrogenation of Benzofurans Catalyzed by a Bulky Ruthenium-NHC complex

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The asymmetric hydrogenation of aromatic compounds is the most straightforward synthetic method to obtain saturated cyclic molecules, which are present in many biologically active systems. A highly versatile chiral ruthenium NHC catalyst proved to be very effective for the enantioselective hydrogenation of a large series of heteroaromatics[1]. In spite of the extensive structural investigations performed for the hydrogenation of 2-methylbenzofuran[2], the mode of action of the catalyst still remains unexplored.

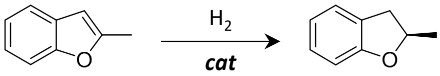

Figure 1: The reaction studied

The aim of our theoretical study was to gain a better insight into the structure of the active catalyst as well as, to elaborate the reaction mechanism for this system.

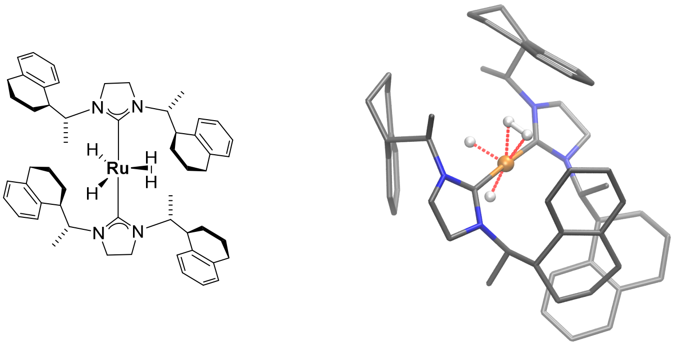

Figure 2: Proposed and computed structures of the active catalyst.

Several isomers and conformations have been considered to identify the most likely form of the catalyst. We proposed a feasible reaction mechanism and all elementary steps and reaction intermediates have been calculated. The most important feature of this system is the different structure of the catalyst toward the two enantiomeric products (“pocket” vs. “flat” conformation). We showed that in spite of the complex conformational space of the bulky ligands of ruthenium these typical forms are inherited through the whole mechanistic pathway. The experimental enantioselectivity has been qualitatively reproduced by our calculations[3].

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Multi-slit-type interference in carbon 2s photoionization of polyatomic molecules

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A recent study on the inner-valence MOs of a series of simple hydrocarbons with two centers has shown that the interference in coherent emission of photoelectrons from these equivalent centers represents the microscopic analogy of the Young's double-slit experiment [1]. This type of interference is related to both electronic and geometrical structure.

In the present work, we extend this research line and we enlighten the first evidence of the multi-slit-type interferences in the C 2s photoionization of several polyatomic molecules: propane, n-butane, isobutane and methyl peroxide. A more complex pattern is observed due to molecular orbital delocalization, blurring the distinction between interference and diffraction. The potential to extract geometrical information is emphasized, as a more powerful extension of the EXAFS technique.

We demonstrate that from the multi-slit interference patterns quantitative conformational analysis, generally outside the capability of photoionization studies, can be addressed, namely the determination of the relative weight of conformers in long-chain hydrocarbons and in a heterosystem (dimethylperoxide).

The experimental results are compared with the theoretical predictions by density functional theory (DFT) calculations. Cross-section calculations have been performed with the linear combination of atomic orbitals (LCAO) B-spline code [2], which provides an accurate solution of the DFT (Kohn-Sham) Hamiltonian for bound and continuum states.

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Exploiting artificial neural networks in simulation of complex ionic chemical environment

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Ab initio molecular dynamics of condensed phase systems featuring charged species rely upon the accurate quantum description of highly complex chemical environment (e.g., various structural patterns, subtle non-covalent interactions and charge transfer processes) at converged statistical sampling. Simulations of chemical reactions in solution are even more challenging due to the larger complexity of the free energy landscapes. Such condensed phase phenomena are ideally suited to drive quantum chemistry out of its comfort zone and combine the power of enhanced sampling MD techniques with the latest sophisticated innovations from quantum machine learning. Atomic potentials based on artificial neural networks (ANN) have been increasingly used to simulate bulk materials, surface adsorption, gas phase reactions or aqueous solutions.[1] ANN are capable of describing high dimensional PES at the same accuracy as the reference quantum chemical method but at a computational cost comparable to classical force field simulations.[2]

In the present work, we exploit ANN potentials based on PBE and PBE0 to model complex catalytic process in condensed phase. Particular emphasis is placed on the accurate description of subtle ion-solvent interactions under various compositions and thermodynamic conditions. Our simulation protocol is generally applicable to model thermodynamic and structural properties of condensed phase systems and chemical reactions in a complex environment. The synergic application of state-of-the-art algorithms such as multiple timestepping[3], replica exchange sampling, farthest point and CUR feature selection[4] accelerates the sampling of the reference training set and affords stable simulations with relevant time scales.

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Fragment-Based Restricted-Active-Space Configuration Interaction with Second-order Correction Embedding for Periodic Hartree-Fock Wave Function

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We present an embedding method for restricted-active-space configuration interaction with second-order perturbative correction (RASCI-PT2)[1] embedded in the periodic Hartree-Fock (HF) wave function. The method allows us to calculate the electronic structure of localized feature for fragment in periodic systems. We first outline the implementation of embedding scheme employing Crystal17[2], Cryscor[3], and Q-Chem[4]. To evaluate our embedding method, we calculated the energy profile of single-bond dissociation of carbon-fluoride of fluorinated graphane, and the electronic excitation energies in covalent-organic framework. The results suggest that RASCI-PT2 embedded in HF wave function can be a promising tool for studying local properties of solid state.

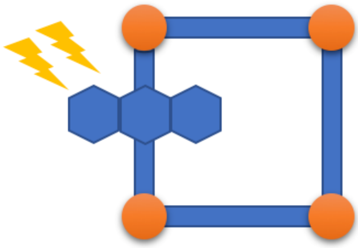

Figure 1: Example for a target system: a photoactive center in a periodic covalent-organic framework (COF).

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Combining DMRG and coupled cluster approaches for static and dynamic correlation

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In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favorable scaling, it is in practice not suitable for computations of dynamic correlation. Recently we presented a method for accurate "post-DMRG" treatment of dynamic correlation based on the tailored coupled cluster (TCC) approach [2] in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas dynamic correlation is incorporated through the framework of the CC theory [3, 4]. In order to overcome the computational scaling bottleneck of traditional CC methods, we have developed an implementation of the DMRG-tailored coupled cluster method [6] based on the local pair natural orbital formalism (LPNO) [7] and domain LPNO (DLPNO) [8] approaches.
However, the tailored CC approach is based on a single reference determinant and (for a truncated T operator) thus exhibits a certain bias, particularly if several determinants have equal or comparable weight. We have thus extended the tailored-CC idea to the Hilbert-space multireference CC, where a small CAS1 space contains these most strongly contributing determinants, while a relatively large CAS2 space is treated at the DMRG level. The amplitudes in the Jeziorski-Monkhorst ansatz over CAS1 are then tailored within the CAS2 space employing a multireference generalization of the CC amplitude analysis.
Motivated by the excitation subalgebra CC approach recently introduced by Kowalski [9], we suggest an intertwined iterative combination of DMRG and CC, where DMRG represents the first iteration, tailored CC the second one, and DMRG with a Hamiltonian similarity-transformed by the T_{ext} operator obtained from previous step the third one etc. Due to the subalgebra CC properties [9], for untruncated T operator and full DMRG bond dimension this procedure converges to full CI. We developed a pilot implementation of this approach for unlimited rank of the T operator and present first numerical results.

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Time-Dependent Linear Response for Coupled Electron-Boson Systems

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Time-dependent linear response theory[1] is the most widely used approach for calculating excitation energies of electronic systems. In doing so, the Casida equation[2] is solved. This formalism is not restricted to electronic systems, but can also be applied to systems coupled to other fermionic particles (e.g. protons[3]), or to bosonic (quasi-)particles, such as photons[4], Drude oscillators, or nuclear vibrations:

$$\begin{pmatrix} \boldsymbol{A}^{\mathrm{I}} & \boldsymbol{A}^{\mathrm{I}\leftrightarrow\mathrm{II}} & \boldsymbol{B}^{\mathrm{I}} & \boldsymbol{B}^{\mathrm{I}\leftrightarrow\mathrm{II}} \\ (\boldsymbol{A}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{\dagger} & \boldsymbol{A}^{\mathrm{II}} & (\boldsymbol{B}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{\dagger} & \boldsymbol{B}^{\mathrm{II}} \\ -(\boldsymbol{B}^{\mathrm{I}})^{*} & -(\boldsymbol{B}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{*} & -(\boldsymbol{A}^{\mathrm{I}})^{*} & -(\boldsymbol{A}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{*} \\ -(\boldsymbol{B}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{\mathrm{T}} & -(\boldsymbol{B}^{B})^{*} & -(\boldsymbol{A}^{\mathrm{I}\leftrightarrow\mathrm{II}})^{\mathrm{T}} & (-\boldsymbol{A}^{\mathrm{II}})^{*} \end{pmatrix} \begin{pmatrix} \boldsymbol{x}^{\mathrm{I}} \\ \boldsymbol{x}^{\mathrm{II}} \\ \boldsymbol{y}^{\mathrm{I}} \\ \boldsymbol{y}^{\mathrm{II}} \end{pmatrix} = \hbar\omega \begin{pmatrix} \boldsymbol{x}^{\mathrm{I}} \\ \boldsymbol{x}^{\mathrm{II}} \\ \boldsymbol{y}^{\mathrm{I}} \\ \boldsymbol{y}^{\mathrm{II}} \end{pmatrix} \tag{1}$$

Hereby, the matrices and vectors are defined in a basis of single-particle excitations. The $\boldsymbol{A}$ matrices and $\boldsymbol{x}$ vectors contain information about occupied-virtual excitations, while the $\boldsymbol{B}$ matrices and $\boldsymbol{y}$ vectors contain information about virtual-occupied excitations (i.e. deexcitations). The superscript denotes whether a submatrix/subvector contains contributions from subsystem I or II or whether it is an interaction term ($\mathrm{I} \leftrightarrow \mathrm{II}$). An extension to additional subsystems is straightforward.
Starting from a mean-field treatment, the A and B matrices consist of the occupied-virtual elements of the derivative of the Fock matrix w.r.t. the density matrix. With this methodology, e.g. environment effects can be accurately captured at a low computational cost.

On the poster, theoretical aspects, details of a general implementation and sample applications using the Hartree–Fock approximation for the electrons will be shown.

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Accelerating high-accuracy electronic structure theory

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Studying the electronic structure of systems containing more than a few atoms is computationally very demanding. For the most accurate methods, doubling the system size leads to over a 100-fold increase in the time and resources required. Thus, to investigate the behaviour of large-scale problems accurately requires the development both of new theories, and new technical approaches to their computation. Much research has recently been put in to finding linear-scaling coupled cluster approaches, with increasing success [1].

We present details on how our recently developed ALMO+RPA method [2] for intermolecular interactions can be extended to arbitrary levels of accuracy through stochastic methods. Moreover, we demonstrate how this lends the method to massive parallelisation, and the concomitant speed-ups this generates. In this way, we find it is possible to deal with solvated complexes of thousands of small molecules with coupled cluster level accuracy, using minimal computational resources. Extensions in the future will look towards using multilayer approaches to deal with even larger systems.

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Insights into Chemistry through the Computation of Free Energy Hot-Spots

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Predicting free energies is one of the key challenges in modern quantum chemistry [1]. For small, unimolecular systems this is usually done via a frequency analysis of the molecule using quantum mechanics (QM) calculations. For large systems, usually free energy differences computed from sampled energies are considered by applying, e.g., Bennett's acceptance ratio method [2]. The interpretation of free energy results is in most cases not straightforward, because it is not possible to distinguish different contributions [3] and, therefore, to understand the underlying effects (e.g., bond weakening, sterical clashes, new non-covalent interactions) causing the free energy to change. Based on an approach originally introduced by Berens *et al.* [4] to estimate quantum corrections to thermodynamic properties, we present a method [5,6] that calculates the vibrational part of the free energy from the vibrational density of states function and locates changes in the potential energy surface. Those are the so-called hot-spots, which we interpreted as the locations causing the overall free energy change. We show the performance of our method for two examples. The first uses classical mechanics to describe the binding of a protein and an inhibitor, where our method identifies all relevant interactions between protein and inhibitor. The second example uses quantum mechanics to identify all atoms affected by the anomeric effect in glucose. We expect, our method to be generally applicable for visualizing and understanding changes between two states within molecular transformations.

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Non-orthogonal configuration interaction to study singlet fission

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We have developed a variation of the non-orthogonal configuration interaction (NOCI) approach [1-2] to study the interaction between excited states on neighbouring molecules in a cluster. In our implementation, the NOCI wavefunction is written as a linear expansion of many electron basis functions (MEBFs), which are spin-adapted, antisymmetrized products of multi-determinantal molecular wavefunctions. Each molecular electronic state is expressed in its own set of optimized orbitals. NOCI can account for electron correlation and orbital relaxation in an efficient way, gives short wavefunction expansions, and allows for a clear chemical interpretation in terms of the localized molecular states.

We have drastically reduced the computational bottlenecks that arise due to the use of non-orthogonal orbitals for large molecular systems. We decreased the number of integrals by around 100 fold by expressing the integrals in a reduced common molecular orbital basis for the different electronic states [3]. The calculation was simplified further by including only the relevant determinant pairs. Hybrid OpenMP/MPI parallelization and GPU acceleration was used to speed up the calculations.

We present here our results of using NOCI to study energy transfer in singlet fission (SF), a molecular process that has been found to be a promising way to enhance the efficiency of organic photovoltaics [4]. Using NOCI we calculate the effective coupling between the initially photo-excited state and the state describing the two triplet excitations that are coupled into a singlet. Our results on using NOCI to study SF are very promising [5] and show that the method can also be used to study charge transfer processes.

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Ultra low energy scattering and chemistry with the R-matrix

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New developments in experimental methods allow for the routine production of ultracold (microkelvin) atoms and molecules. This has facilitated the study of chemical reactions involving only a small number of partial waves, allowing for unprecedented control over elastic and inelastic collisions and ultracold chemical reactions.

We are developing a new program, RmatReact, which uses the R-matrix and associated methodology to accurately simulate heavy particle collision events at these ultracold temperatures [1]. The method divides space into an inner and outer region along the reaction coordinate. The only input required is a suitable potential energy function. Information about the bound rovibrational states in the inner region, specifically eigenenergies and wavefunctions, which are generated from variational nuclear motion programs built for high-accuracy spectroscopy, is used to generate information about the scattering event in the outer region. The results which are produced are scattering observables such as the scattering length, the S-matrix and the cross sections for different processes.

With this method, calculations can be done inexpensively at many different scattering energies, allowing for high-resolution plots of these observables and the characterisation of long-lived quasi-bound states (resonances). Initial results generated using this code have concentrated on atom-atom collision such as Ar – Ar [2] and O – He using code Duo [3] for the inner region. Development of the method for atom – diatom collisions, including reactive one, is also in progress [4].

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Non-Hermitian Quantum Chemistry: Connecting Excited States through the Complex Plane

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Electronic excited states are central to processes across many areas of science. In principle, excited-state energies are given by the discrete solutions of full configuration interaction (FCI) in a complete basis set, however accurately determining these energies remains a major challenge in theoretical chemistry. Alternatively, higher energy stationary states of approximate methods — including non-linear self-consistent field (SCF) approaches and truncated configuration interaction (CI) — can themselves be interpreted as approximations to excited states, although our general understanding into the nature of these solutions remains surprisingly limited. In this work, we present an entirely novel approach for exploring excited stationary states across quantum chemistry that exploits the properties of non-Hermitian Hamiltonians. Our key idea centres on performing complex analytic continuations of conventional methods that reveal rich and diverse behaviours in the complex plane. For example, by analytically continuing the electron-electron interaction in holomorphic Hartree–Fock theory,[1–3] we expose a hidden connectivity of multiple solutions across the complex plane.[4] In doing so, we reveal that Coulson–Fischer points (where real Hartree–Fock solutions coalesce) behave more generally as non-Hermitian "exceptional point" degeneracies. Finally, we demonstrate how one can exploit this complex topology to naturally evolve a ground-state wave function into an excited-state wave function using a well-defined complex adiabatic connection.

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Real-time response from imaginary-time simulation: Hacking quantum statistics with Path Integral Monte Carlo

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The electric field response is a fundamental property of matter, which in case of atoms and molecules, culminates in polarizability. The static and dynamic multipole polarizabilities are the origins of all kinds of spectral phenomena, such as infrared activity, optical dispersion, and x-ray scattering. Often the full response is indeed divided into electronic and rovibrational effects in the Born-Oppenheimer approximation, which neglects their coupling to each other and the finite temperature. In a recent work [1], we go beyond the Born-Oppenheimer approximation in an ab initio path integral Monte Carlo simulation (PIMC), which enables us to study the combined electronic, rovibrational and nonadiabatic effects on the total dynamic polarizability.

Unfortunately, estimating dynamic properties is a notorious challenge with real-space Quantum Monte Carlo (QMC) methods, such as PIMC. While the variants of QMC excel in complex quantum statistical many-body problems, they usually operate in imaginary time. Theoretically, the generalized susceptibilities, or the quantum correlation functions in the imaginary domain can be analytically continued to yield the real-time response properties. However, the practical implementation is an ill-posed inversion problem, which defies even the most sophisticated methods. Here we focus on a particular numerical approach: Maximum Entropy method (MaxEnt) [2]. While MaxEnt has its flaws, it provides convincing estimates of the exact multipole spectra, dynamic polarizabilities, and accurate van der Waals coefficients of several small atomic and molecular systems.

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Probing chiral properties of medium-to-large organic molecules: The VPT2 approach

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The biological activity of molecules is strongly dependent on their chirality. Understanding this property is thus of critical importance in pharmaceutical industries, but has gained growing interest in other technological applications. Chiral spectroscopies, in particular Vibrational Circular Dichroism (VCD) and Raman Optical Activity (ROA), are the methods of choice to probe and analyze the dynamic and structural characteristic of such molecules.[1] The wealth of information contained in experimental spectra cannot be fully exploited through phenomenological studies, and quantum mechanical simulations are now systematically used to support and complement observations. While the harmonic approximation is often sufficient to assign absolute configurations, it has inherent limitations, which can hinder a detailed analysis of the vibrational properties of a system, like the overestimation of transition energies or the impossibility to reproduce non-fundamental bands. Such issues are often exacerbated by the sensitivity of chiroptical spectroscopies. Significant improvements are obtained by proper inclusion of anharmonic effects. However, the computational cost of such methods has confined them to small molecular systems.

Thanks to hardware improvements and its good cost-accuracy ratio, vibrational second-order perturbation theory (VPT2)[2] can now be applied to the anharmonic simulation of medium-to-large systems.[3,4] Nonetheless, the increase in problem size and structural complexity also worsens the well-known issue of resonances, which can seriously affect the accuracy and reliability of VPT2 results. As a "visual" identification of resonances becomes unpractical, robust automatic procedures are necessary,[5] and their validation requires extensive studies on small- to medium-sized molecules. In this contribution, the importance of a correct identification and treatment of resonances will be illustrated. The impact of the quality of the harmonic approximation, and the underlying electronic structure calculation method will also be considered. The design of a reliable protocol will build the path to systematic application of VPT2 to larger systems, here represented by pinene and artemisinin.

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Thermochemistry and electronic structure properties of cyclacenes using homodesmotic reactions and DFT

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Belt shaped molecules consisting of fused conjugated hydrocarbons are potential nanostructures due to their radially oriented p orbitals and superior optoelectronic properties. $[m]$ Cyclacenes are molecules formed by fusing m membered conjugated rings. $[6]_n$ Cyclacenes are formed by fusing n benzene rings. $[6]_n$ Cyclacenes can be considered as the basic unit of zigzag carbon nanotubes (CNTs)[1]. Chemical Synthesize of $[6]_n$ cyclacenes is very difficult due to their high strain which results from bending of benzene, reactiveness and their predicted open-shell character. If we use molecules with in-built bending, like cyclooctatetraene, it is easier to synthesize belt shaped molecules. But the major concern is change in their electronic properties. In this work, we have studied the thermochemistry and the electronic structure properties of different cyclacenes fused by benzene, cyclobutadiene and cyclooctatetraene using homodesmotic reactions[2] and density functional theory.

Homodesmotic reactions are theoretically proposed reaction schemes in which reactants and products should have equal number of hybridized carbon atoms with 0,1,2 and 3 hydrogens attached to them and equal number of bonds formed between different hybridized carbon atoms. The scheme is devised so as to provide nearly identical chemical environments for hypothetical reactants and products so as to minimize computational errors[3].

(a) $[6.8]_4$ Cyclacene (b) $[8]_8$ Cyclacene

Figure 1: Examples of Cyclacenes studied in this work

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Poster: P1-85

Accurate Electronic Energies by Stochastic Wave Function Sampling and Deterministic Coupled-Cluster and Equation-of-Motion Coupled-Cluster Computations

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One of the main goals of quantum chemistry is an accurate description of ground- and excited-state energetics of increasingly complex polyatomic systems, especially when non-equilibrium structures and systems with stronger correlations are examined. Size extensive methods based on the coupled-cluster (CC) theory and their extensions to excited states via the equation-of-motion (EOM) framework have become *de facto* standards for addressing this goal. In the vast majority of chemistry problems, the CC hierarchy, including CCSD, CCSDT, CCSDTQ, etc., and its EOM counterpart provide the fastest convergence toward the exact, full configuration interaction (FCI), limit, allowing one to capture the leading many-electron correlation effects in a systematic manner by employing particle-hole excitations from a single reference determinant. Unfortunately, computational costs associated with the incorporation of higher–than–two-body components of the relevant cluster and excitation operators, which are required to achieve a fully quantitative description, are often prohibitive. This has created the need for new ideas in this area that do not suffer from failures of perturbative CC methods of the CCSD(T) type in multi-reference situations, while preserving the simplicity of a single-reference formalism. In response to this need, we have proposed a novel, computationally cost-effective strategy for obtaining accurate molecular electronic energetics, equivalent to those obtained with high-level CC methods, such as CCSDT and CCSDTQ, or the exact, FCI, approach, even when wave function quasi-degeneracies become significant, by merging the deterministic CC framework, especially CC(P;Q) [1,2], with the stochastic CI [3,4] and CC [5] Quantum Monte Carlo (QMC) approaches [6]. In this presentation, we discuss our recent progress in this area, including (i) extension of the original work [6] to excited states by using CIQMC propagations to identify higher–than–doubly excited wave function components in deterministic EOMCC computations [7] and (ii) direct recovery of the FCI energetics via cluster analysis of FCIQMC wave functions combined with CCSD-like calculations, in which singly and doubly excited clusters, needed to determine the energy, are iterated in the presence of their three- and four-body counterparts extracted from FCIQMC [8]. Our work toward converging FCI energetics in strongly correlated systems, such as those involved in modeling metal–insulator transitions [9], by combining short FCIQMC runs with inexpensive deterministic CC computations will be discussed as well.

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All-electron relativistic four-component Dirac–Kohn–Sham theory for solids using Gaussian-type functions

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I will present a four-component Dirac–Kohn–Sham theory for obtaining relativistic band structures of spin–orbit-coupled solids. The method was recently developed in our group [1], and uses Gaussian-type orbitals (GTOs) to compactly express all operators in real space. The four-component self-consistent field equation of a translationally invariant system

$$\begin{pmatrix} \mathcal{V}^{LL}(\boldsymbol{k}) & \mathcal{T}(\boldsymbol{k}) \\ \mathcal{T}(\boldsymbol{k}) & \frac{1}{4c^2}\mathcal{V}^{SS}(\boldsymbol{k}) - \mathcal{T}(\boldsymbol{k}) \end{pmatrix} \begin{pmatrix} c_L(\boldsymbol{k}) \\ c_S(\boldsymbol{k}) \end{pmatrix} = \epsilon(\boldsymbol{k}) \begin{pmatrix} \mathcal{S}(\boldsymbol{k}) & 0_2 \\ 0_2 & \frac{1}{2c^2}\mathcal{T}(\boldsymbol{k}) \end{pmatrix} \begin{pmatrix} c_L(\boldsymbol{k}) \\ c_S(\boldsymbol{k}) \end{pmatrix} \tag{1}$$

is then solved in its matrix form in reciprocal space using the restricted kinetically balanced basis. The atom-centered nature of GTOs allows for explicit handling of one-, two-, and three-dimensional periodic systems while avoiding the need to introduce vacuum layers. The spin–orbit coupling is treated variationally, which allows for studying topological insulators as well as spin–orbit-induced splittings of bands in materials containing heavy elements. The GTO-based all-electron methodology makes no assumptions about the electronic density in the vicinity of nuclei, and can be used to calculate core-related properties, such as nuclear magnetic resonance parameters. To enable large-scale relativistic calculations of solids containing thousands of heavy atoms in the simulation supercell, the presented approach exploits fast-multipole methods, and is implemented in the ReSpect program package [2] that uses the quaternion algebra for the time-reversal-adapted basis.

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Unraveling Proton Storage Site and Generic Proton Release Pathway in a Prototype Light-Driven Proton Pump Bacteriorhodopsin

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Understanding the mechanism of proton pumping in the simplest light-driven proton pump, bacteriorhodopsin (bR), is crucial to unveil the proton pumping function of even more complex proton pumps. Yet, despite decades of research various conflicting issues related to the location of excess proton and proton release pathways in bR are still not well understood. By applying state of the art computational techniques we unveil the precise location and chemical identity of the proton release group in addition to discovering the subsequent proton release pathways in bR. The proton release group as discovered from our study satisfies most available experimental results, specially the manifestation of continuum band in the obtained spectra and the associated anisotropic feature that has been experimentally observed only recently. Moreover, we disclose the molecular mechanism and pathway by which the stored proton, being stored in an ultra-strong centered H-bond, is released to the extracellular bulk. We believe that the insight obtained from our study can be utilized to understand the mechanism of ion pumping of other more complex membrane transporters.

Unraveling Exciton Dynamics in 2D Van der Waals Heterostructures

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Two-dimensional (2D) van der Waals (vdW) heterostructures offer a fascinating platform to pursue fundamental science and novel device applications. Owing to quantum size confinement and reduced dielectric screening, electron-electron interaction and excitonic effect are prominent in 2D materials, which could dominate their electron and exciton dynamics. Recent experiments have revealed ultrafast charge (~100 fs) and energy (~1 ps) transfer dynamics in transition metal dichalcogenides (TMDs) heterostructures, which is surprising giving the strong electron-hole binding of the interlayer excitons. Most theoretical calculations to understand the experiments were performed based on local and semi-local exchange-correlation functionals, thus cannot capture the excitonic effect accurately. In this talk, I will introduce a first-principles method that combines non-adiabatic molecular dynamics (with the fewest switch surface hopping algorithm) and linear-response time-dependent density functional theory. Importantly, the method is formulated in the planewave bases and PAW pseudopotentials with range-separated hybrid functionals. As a result, the method can capture the excitonic effect accurately in extended 2D heterostructures. Using this method, we can shed light on the ultrafast charge transfer dynamics in TMD vdW heterostructures and elucidate the role of “hot” excitons in promoting ultrafast charge transfer despite the momentum mismatch in twisted heterostructures. We can also examine the properties of interlayer and intralayer excitons trapped by the moiré superlattices in the twisted heterostructures, and tune their properties and lifetimes by changing the twist angle, pressure and electric field.

Structure Optimisation of Large Transition Metal Complexes with Extended Tight-Binding Methods

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Computer-aided theoretical investigations of large organometallic complexes are generally limited by the sheer size of real systems often consisting of hundreds to thousands of atoms. Accordingly, the development and evaluation of fast semiempirical quantum chemistry methods is indispensable. Here we report on the capability of the recently developed GFNn-xTB[1,2] methods , which are generally applicable for a large part of the periodic table including also lanthanoids[3] to perform full quantum mechanical geometry optimisation of large transition metal complexes and supramolecular organometallic structures. The results for a newly compiled benchmark set of 145 diverse closed-shell transition metal complexs including all transition metals up to Hg are presented. Additionally, the GFNn-xTB[1,2] methods are tested on established benchmark sets of organometallic reactions[4] and cross-checked for large and difficult show cases.

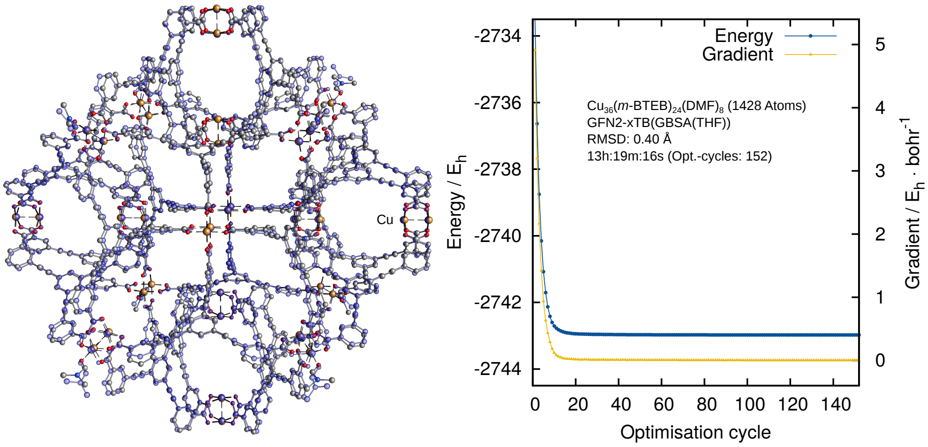

Figure 1: GFN2-xTB geometry optimisation of a large organometallic keplerate cage.[4]

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Combining the Density Matrix Renormalization Group with Selected Configuration Interaction

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The density matrix renormalization group (DMRG) is a powerful method for solving quantum chemical systems with significant static correlation [1]. However, DMRG becomes too expensive for systems with very large active spaces (number of orbitals). Here, we propose to combine selected configuration interaction (SCI) techniques [2] with the DMRG. This is done by grouping orbitals located at the same atom into one site in the DMRG. The number of atoms then corresponds to the number of sites. Accordingly, the underlying representation of the DMRG describes selected many-body configurations instead of orbital occupations as is the case in conventional DMRG. The previously proposed active space decomposition (ASD) DMRG [3] is similar, but fundamentally differs by a restricted-active-space-based configuration selection and by using whole molecules as sites. Our SCI-based DMRG requires much smaller bond dimensions than conventional DMRG and is more general than ASD-DMRG. Preliminary results on hydrogen chains are presented.

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On the Synergy of Matrix-Isolation Infrared Spectroscopy and Vibrational Configuration Interaction Computations

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Numerous developments in quantum chemistry promise an economic and flexible, yet, accurate access to Potential Energy Surfaces (PESs) of polyatomic molecular systems, where the design of global PESs is cumbersome and expensive. A prominent field where accurate PESs are needed is Vibrational Structure Theory, *e.g.*, for the calculation of vibrational states of molecular systems by variational methods for solving the time-independent nuclear Schrödinger equation, *i.e.*, Vibrational Self Consistent Field (VSCF) and Vibrational Configuration Interaction (VCI). Within a variety of authors working in this field, we find the most versatile implementations in the MOLPRO software package [1] with the PES generator and VSCF/VCI algorithms by Rauhut et al. [2,3]. In this work, we recorded high-resolution spectra by Argon and Neon Matrix-Isolation Infrared (MI-IR) Spectroscopy, a technique that suppresses molecular rotation to access pure vibrational spectra. We perform VSCF/VCI computations on *ab initio* multi-mode PESs to support assignment of the MI-IR spectra, which, vice versa, validate the accuracy of the computations. With this iterative spectroscopic characterization, we are able to solve some inconsistencies in the well-studied spectrum of the water monomer [4] and to confirm the experimentally implied molecular picture by quantum chemical calculations. We extend this combined experimental and computational approach to compounds, where a precise characterization is highly relevant, *e.g.*, key components in the activation of carbon dioxide or volatile organic compounds found in the atmosphere.

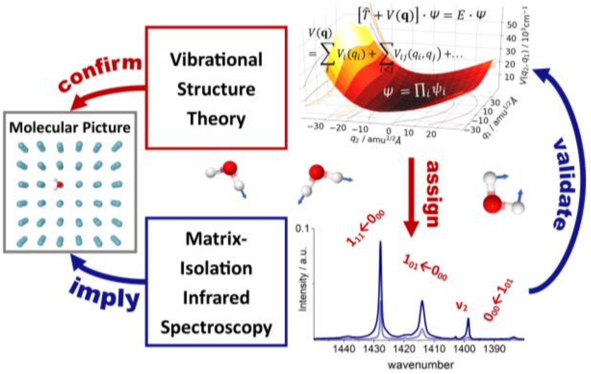

Figure 1: Schematic representation of the iteration between theory and experiment that take place during characterization of molecules by spectroscopy.

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Single-Hessian thawed Gaussian approximation: The missing rung on the ladder

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To alleviate the computational cost associated with on-the-fly ab initio semiclassical calculations of molecular spectra, we propose the single-Hessian thawed Gaussian approximation [1], in which the Hessian of the potential energy at all points along an anharmonic classical trajectory is approximated by a constant matrix. The spectra obtained with this approximation are compared with the exact quantum spectra of a one-dimensional Morse potential and with the experimental spectra of ammonia and quinquethiophene. In all cases, the single-Hessian version performs almost as well as the much more expensive on-the-fly ab initio thawed Gaussian approximation [2, 3, 4] and significantly better than the global harmonic schemes. Remarkably, unlike the thawed Gaussian approximation, the proposed method conserves energy exactly, despite the time dependence of the corresponding effective Hamiltonian, and, in addition, can be mapped to a higher-dimensional time-independent classical Hamiltonian system. We also provide a detailed comparison with several related approximations [5, 6] used for accelerating prefactor calculations in semiclassical simulations.

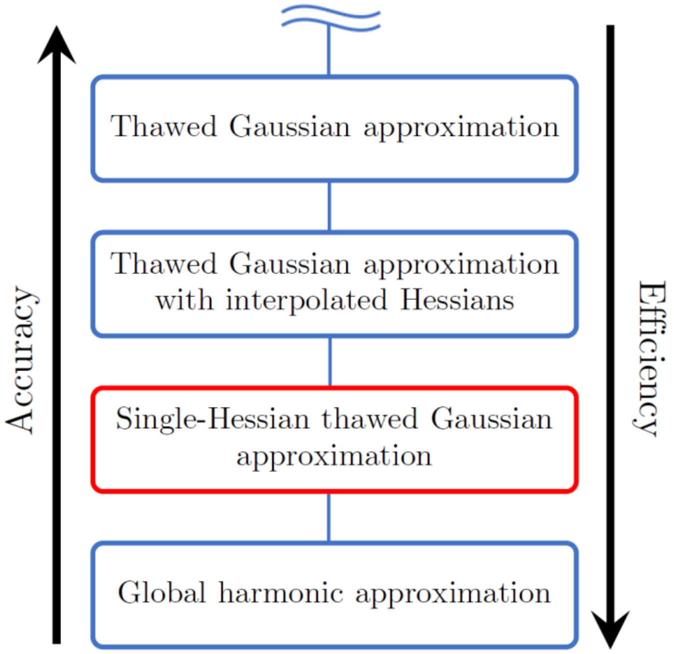

Figure 1: Hierarchy of several semiclassical wavepacket methods for simulating vibrationally resolved electronic spectra.

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A Theoretical Study on the Gas- and Aqueous-Phase Photodegradation and Thermal Decomposition Channels of Pyruvic Acid

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Pyruvic acid (PA) is a key intermediate in the keto-acid chemistry of atmospheric aerosols. Currently, there is still a lack of fundamental understanding of the PA degradation processes in both gas and aqueous phase. In this work, several pathways leading to vinyl alcohol, acetaldehyde, and acetic acid were explored. These were determined by density functional theory (DFT) using B3LYP and coupled cluster method with singles and doubles correction using the second-order Møller–Plesset perturbation theory structures. The solvation model based on density (SMD) was used for the aqueous phase calculations. The Dunning-style cc-pVTZ basis set was used for all calculations. The most accessible thermal decomposition pathway is through the hydroxymethylcarbene (CH_3COH) intermediate, with an overall barrier height of 42.19 and 45.92 kcal/mol for gas and aqueous phase, respectively. All the pathways favor decomposition in solvation except for the acetaldehyde pathways. Moreover, using the time-dependent DFT, only the CH_3COH channel allows photodegradation to proceed within the 300-380 nm through the first triplet and singlet excited states.

DFT-calculated Magnetic Parameters of Physiological Copper(II) Complexes with L-asparagine and L-histidine: A Tool for Verification of Predicted Lower-energy Conformers in Aqueous Solution

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The copper(II) complexes chelated with two amino acids have been isolated from normal human blood serum and reported to be part of an exchangeable serum pool for copper [1,2]. It was shown that a majority of these physiological compounds were Cu^{II} complexes with L-histidine (L-His) in the form of electrically neutral bis(L-histidinato)copper(II), and ternary complexes favorably with L-asparagine (L-Asn), L-threonine, and L-glutamine. The experimental studies of these physiological complexes were intensive during the 1970s through the 1980s. However, they did not determine the exact structures of the complexes in solutions. Our recent computational study resolved that missing piece of information for bis(L-asparaginato)copper(II) [Cu(L-Asn)$_2$] and (L-histidinato)(L-asparaginato)copper(II) [Cu(L-His)(L-Asn)] by exploring their structural properties and energy landscapes using the density functional theory (DFT) with the B3LYP functional [3]. Systematic conformational analyses in the gas phase and in implicitly modeled aqueous surroundings using a polarizable continuum model located the low-energy conformers, and rationalized the effect of noncovalent interactions on the coordination modes and overall geometries of the complexes.

The predicted lower-energy aqueous structures with various combinations of the in-plane and apical donor atoms are used for DFT calculations of the g-factor and hyperfine coupling constants (HFCC) for a quantitative comparison to experimental electron paramagnetic resonance (EPR) data [4-6]. The calculated isotropic g_{iso} and the most variable g_z component of the $\mathbf{g}$ tensor, HFCC of the ^{63}Cu (A^{Cu}) and ^{14}N (A^{N}) centers were compared with their values obtained from the EPR spectra measured in aqueous solutions. The best match between the experimental and calculated magnetic parameters was obtained for the conformers in the coordination modes with the lowest Gibbs free energy values, and an apical oxygen atom (intramolecular or from a water molecule). A smaller $A^{\mathrm{N}}_{\mathrm{iso}}$ is calculated for the *trans* than *cis* conformers, while the B3LYP $A^{\mathrm{Cu}}_{\mathrm{iso}}$ values are very similar for the *trans* and *cis* conformers with the same coordination number. Our EPR interpretation points to the conclusion that in aqueous solution, a water molecule can place itself at the apical Cu^{II} position if it is free.

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Acknowledgment: This work was supported by the Croatian Science Foundation under the project IP-2014-09-3500.

Diagrammatic Coupled Cluster Monte Carlo

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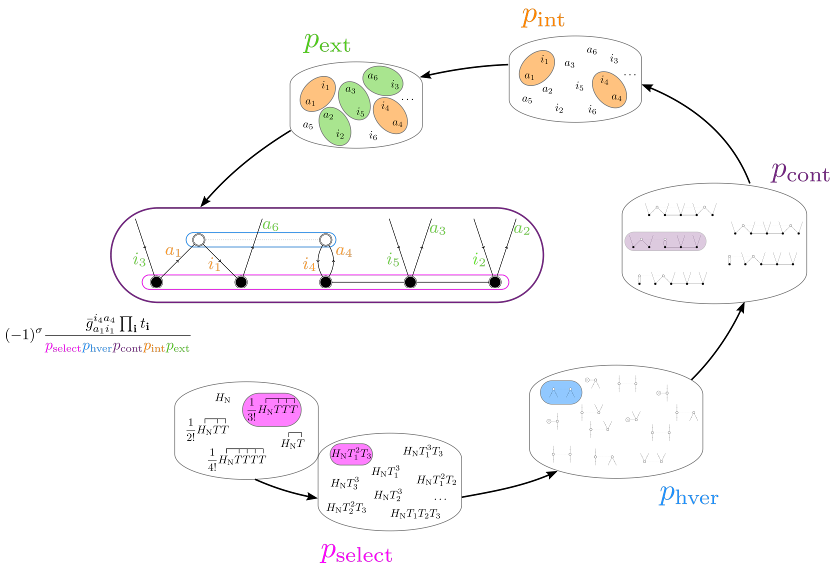
The coupled cluster model is arguably the most effective approximation for many-electron wavefunctions in weakly correlated systems. The model provides a systematically improvable hierarchy of approximations to the exact, full configuration interaction solution. Within a polynomial, rather than exponential, computational scaling, coupled cluster achieves size extensive and consistent results. This polynomial scaling remains however a challenge for its widespread application.

Monte Carlo sampling can circumvent the scaling wall, while remaining fully general with respect to truncation in the excitation hierarchy: an appealing feature when compared to other low-scaling, deterministic approaches.

We present the *diagrammatic coupled cluster Monte Carlo* (diagCCMC) algorithm that solves the linked equations of coupled cluster theory. We sample the connected expansion of the similarity-transformed Hamiltonian generating coupled cluster diagrams on the fly [1]. Results are thus rigorously size-extensive and consistent, even in the presence of stochastic noise. This affords a representation of noninteracting systems with a constant memory cost and reduced CPU cost. The algorithm can leverage locality without additional assumptions.



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A Subquadratic, Pair Atomic Resolution of the Identity-Based SOS-AO-MP2 Implementation in ADF

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We present a production level implementation of pair atomic resolution of the identity (PARI)[1] based second-order Møller–Plesset perturbation theory (MP2) in the Slater type orbital (STO) based Amsterdam Density Functional (ADF)[2] code[3]. Furthermore, we describe a subquadratically scaling, atomic orbital based spin-opposite-scaled (SOS)[4] MP2 approach with a very small prefactor[3], being order-N in memory. Due to a worst-case scaling of $\mathcal{O}(N^3)$, our implementation is very fast for small- as well as for medium- and large-sized systems and shows an exceptionally early crossover to canonical, global density fitting based SOS-MP2. We report wall clock times for computations on realistic three-dimensional molecules and show, that triple-ζ quality calculations on molecules of several hundreds of atoms are only a matter of a few hours on a single compute node. In all considered cases, the computational bottleneck is the SCF, whereas the post-SCF energy correction can be calculated to the price of a few SCF cycles.

To demonstrate the accuracy of our implementation, we report systematic benchmark results for dimerization energies and relative conformational energies. Our results show mean absolute deviations to canonical, basis set extrapolated MP2 reference values of less than 1 kcal/mol when STO basis sets of triple-ζ-quality are used.

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A path integral molecular dynamics study of muoniated acetone radicals

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Muonium (Mu) atom is formed by a positive muon (μ^+) and an electron, where the mass of μ^+ is much smaller than that of a proton and Mu atom has larger nuclear quantum effect than hydrogen. Muoniated radicals are used to muon spin resonance (μSR) by using large magnetic moment of μ^+. μSR technique provides the determination of hyperfine structures of muoniated radicals, which is characterized by the reduced muon hyperfine coupling constant (A_μ') on a radical. The experimental measured A_μ' value of muoniated acetone radical (Mu-ACE, Figure 1) is found to be 8.56 MHz at 300 K [1], and to be smaller as the temperature decreases [2]. However, theoretical A_μ' value for Mu-ACE is calculated to be -5.8 MHz by static optimization calculation [2] and it does not reproduce experimental A_μ' values because it does not include the nuclear quantum and thermal effects. We therefore performed *ab initio* path integral molecular dynamics (PIMD) simulation, which can include these effects, to reproduce A_μ' value of Mu-ACE and explain the temperature dependence of A_μ'.

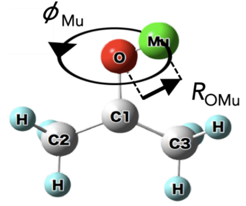
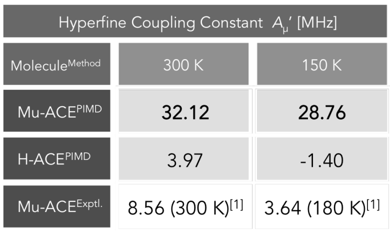


Figure 1: The molecular structure of Mu-ACE.

We performed on-the-fly *ab initio* PIMD simulation with O3LYP/6-31+G level. We used the massive Nosé-Hoover chain thermostat to control the system temperature. We also calculated hydrogenated acetone radical (H-ACE) to compare with Mu-ACE. The numbers of beads for Mu-ACE and H-ACE were 64 and 16, respectively. Imaginary-time step sizes for these simulations were 40 asec/step and 0.1 fsec/step, respectively. The number of total time steps was 95,000 steps for both simulations.

Table 1 shows the experimental and theoretical A_μ' values. Our A_μ' values at 300 K are computed as 32.1 MHz and 3.97 MHz for Mu-ACE and H-ACE, respectively, and our results qualitatively reproduced the relationship between A_μ' of Mu-ACE and H-ACE for corresponding experimental values. This is caused by increase of spin density on Mu atom due to both "neutral dissociation of Mu atom from acetone molecule" and "rotation of Mu atom around C1-O bond" using large nuclear quantum and thermal effects [3]. Temperature dependence and structural discussion will be reported in poster presentation.

Table 1: Summarized A_μ' values for Mu-ACE.



Hyperfine Coupling Constant A_μ' [MHz]		
Molecule^{Method}	300 K	150 K
Mu-ACE^{PIMD}	32.12	28.76
H-ACE^{PIMD}	3.97	-1.40
Mu-ACE$^{Exptl.}$	8.56 (300 K)[1]	3.64 (180 K)[1]

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Molecular dynamics simulation study of the drug resistance mechanism of hepatitis C virus NS3/4A to Paritaprevir due to D168N/Y mutations

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Abstract:

Hepatitis C virus (HCV) NS3/4A protease is an attractive target for the development of antiviral therapy. However, drug resistance is a major problem since this can limit drug efficacy. Understanding of drug-resistance mechanism is therefore very important for the guidance of further design high efficiency and specificity antiviral drug. Paritaprevir is an attractive inhibitor with IC_{50} value of 1.0 nM against HCV NS3/4A protease genotype 1a [1]. Although it shows good potency towards the wild-type strain, the D168Y variant was found to confer the highest level of resistance (219). In this work, molecular dynamics simulations of paritaprevir complexed with wild-type and two mutated (D168N and D168Y) strains were carried out. Strong hydrogen bonding interactions between protein and ligand were observed in the wild-type complex while the mutant systems show relatively weak interaction. Moreover, the salt-bridges between residues 168 and 155 were observed in only the wild-type system. This should be responsible for the large conformation changes of the binding pocket in D168N/Y mutants. The per-residue free energy decomposition suggests that the key residues involved in inhibitor binding were residues Q41, H57, V132, K136, S139, R155, A156 in the NS3 domain. Detailed information could be useful for the further design of high potent anti HCV NS3/4A inhibitors.

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New Developments in Fragment-Based Quantum Chemistry

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We describe several fragment-based approaches with the potential to extend quantum chemistry to very large systems. The first of these is an "extended" version of symmetry-adapted perturbation theory (XSAPT) that can be applied to compute benchmark-quality intermolecular interaction energies in noncovalent clusters and assemblies.[1] This method is both more accurate and less costly than supramolecular density functional theory. The XSAPT method naturally includes nonadditive polarization effects and we have recently extended it to include nonadditive many-body dispersion (MBD) as well.[2] The resulting XSAPT+MBD method provides ~ 1 kcal/mol accuracy in calculations with hundreds of atoms and thousands of basis functions. In a second project, we have developed a general framework for fragment-based quantum chemistry that we call the generalized many-body expansion (GMBE),[3,4,5] which we have recently extended to *ab initio* molecular dynamics simulations. By introducing a variational framework for the GMBE, we derive a fragment-based method that preserves the variational nature of the self-consistent field method (SCF), even when the subsystem SCF calculations are embedded in an electrostatic (point-charge) representation of the entire system.[6] This formalism naturally leads to charge-response contributions to the Fock matrix (which have often been neglected in practice), although solution of coupled-perturbed SCF equations is not required. We show that several other fragment-based methods that do not consider the charge-response contributions to the analytic gradient result in catastrophic failure of energy conservation in fragment-based *ab initio* molecular dynamics simulations.

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Poster: P1-100

Dispersion Energy of Symmetry-Adapted Perturbation Theory from the Explicitly Correlated F12 Approach

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Methods of the explicitly correlated F12 approach are applied to the problem of calculating the uncoupled second-order dispersion energy, $E^{(20)}_{\text{disp}}$, in symmetry-adapted perturbation theory (SAPT). The accuracy of the new method is tested for noncovalently bound complexes from the A24 data set [1] using standard orbital basis sets aug-cc-pVXZ supplemented with auxiliary aug-cc-pVXZ_OPTRI sets [2]. For near equilibrium geometries, it is possible to recover the dispersion energy with average relative errors consistently smaller than 0.1% (with respect to the CBS extrapolated limit estimated from regular orbital calculations). This level of accuracy is achieved already in the basis set of a triple-ζ quality, when a Slater-type [3] correlation factor $\exp(-0.9r_{12})$ is combined with variant C of the F12 approach. The explicitly correlated approach clearly outperforms regular orbital calculations in the basis set of quintuple-ζ quality (average relative errors of 1%).

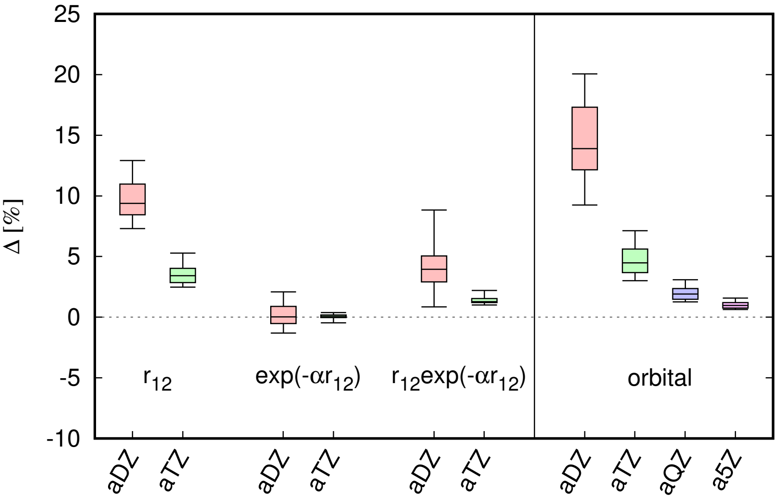

Figure 1: Relative percent errors of the $E^{(20)}_{\text{disp}}$ *calculated for dimers from the A24 data set. [4]*

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Non-variational induced Multipoles for Polarizable Force Fields: Theory and Implementation for Molecular Dynamics Simulations

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Describing electrostatic polarization effects in Classical Molecular Dynamics simulations is an ongoing field of research aiming to make molecular simulations more accurate and realistic. Polarization effects are modelled by introducing induced charges, dipoles or in general multipoles, according to the specific model adopted, arising from intra- and inter-molecular electrostatic interactions. All existing polarization models can be considered variational since the induced multipoles are obtained by minimizing a polarization energy functional: this feature allows an easy evaluation of energy gradients required to perform Molecular Dynamics simulations, as the classical Hellman-Feynman theorem can be invoked. In the case of non-variational models, where the induced multipoles are not obtained by minimizing the polarization energy, energy gradients are formally cumbersome to compute as the multipolar response term needs to be evaluated. We here present a Lagrange formalism allowing the evaluation of energy gradients for non-variational polarization models at a computational cost comparable to that for variational ones. The theory is implemented and tested for the recently proposed Bond Capacity model which introduces polarization at the charge-level [1]. The model is implemented in the Tinker-HP package and long-range electrostatic interactions are treated with the Smooth Particle Mesh Ewald Method [2].

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Relativistic four-component study of through–space spin–spin coupling constants

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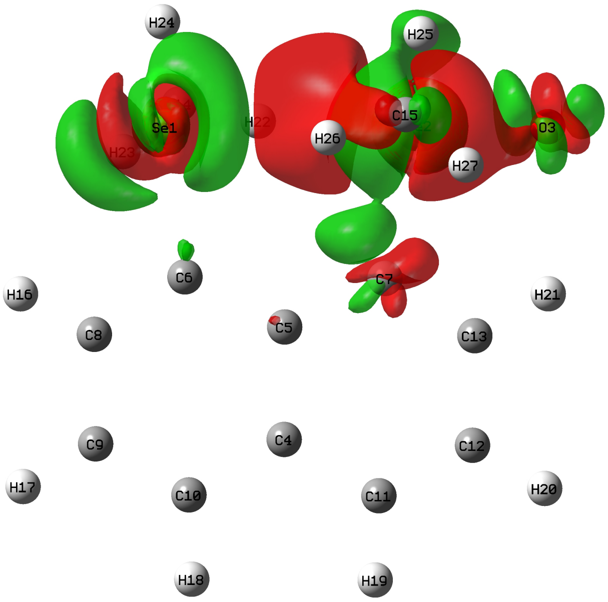
Four-component approach at the density functional level of theory is used to study and visualize through-space NMR spin-spin coupling constants (SSCC). The values of SSCCs of the type Se-Se, Se-Te and Te-Te in three similar molecules determined in the relativistic and nonrelativistic approach are compared. We discuss the first-order current densities induced by the nuclear magnetic dipoles, and different possibilities to visualize the relativistic effects are considered.



Se-Se coupling in peri-substituted naphthalene, $\vec{j}^{Se2,z} \cdot \vec{A}^{Se1,z}$.

MJ acknowledges support by National Science Centre (Poland) grant 2016/21/B/ST4/03904.

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Potential energy Surface for the ground electronic state of SSiH

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Sulfur-bearing molecular systems have attracted the interest of the astrophysical particularly after been observed in ISM and circumstellar regions [1]. This work presents an analytical function for the potential energy surface (PES) of the SSiH. The PES is constructed in the frame of the many-body expansion (MBE)[2]; dividing also each term into two-parts as proposed by Aguado and Paniagua [3]. *Ab initio* calculations, were carried out using Molpro 2012/2015 suite of programs [4]. Multi-reference configuration interaction with Davidson corrections, using the full valence complete-active-space self-consistent field wave function as reference was followed in the electronic structure calculations. Dunning basis sets AVTdZ and AVQdZ were used together with a three parameter scheme to extrapolate to the complete basis set limit. Topological features and exploratory dynamics calculations are discussed.

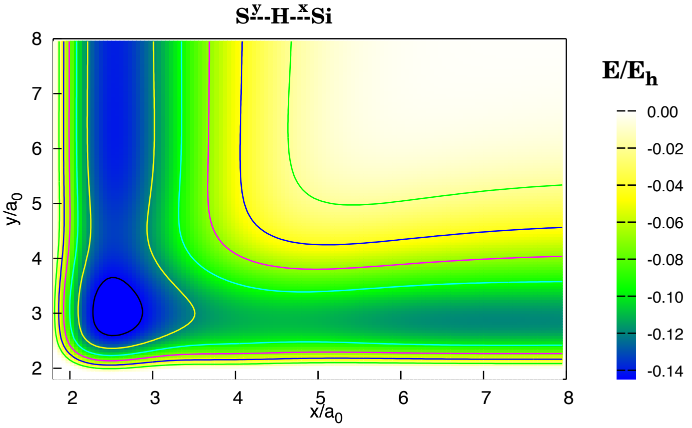

Figure 1: Contours plot for the analytically represented SSiH PES. The linear aproach of the sufur atom to the HSi molecule is depicted. Global minimum and saddle points can be viewed.

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Structure Activity Relationships for Carbonyl Photolysis

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Carbonyls are among the most abundant and photoactive volatile organic compounds (VOCs) in the atmosphere. Their varied, complex structures pose a challenge to atmospheric chemistry models. Experimental photolysis paramaters are available for small prototypical molecules [1], however this data does not cover all reaction channels and is missing larger abundant species.

Atmospheric models circumvent this lack of data by applying the same photolysis parameters from one molecule to all other molecules of that type, *e.g.* the photolysis rate of butanal is used for all linear aldehydes [2]. Such approaches do not fully account for the complex photochemistry of the carbonyl moiety, where small structural changes can alter photolysis rates, accessible electronic surfaces, or even which products are formed.

In this work theoretical chemistry is used to explore the photophysics of the carbonyl moiety as a whole, on all relevant electronic states (S_1, T_1, & S_0), and derive fundamental structure activity relationships (SARs) to rationalise the photochemistry of the diverse carbonyl species shown in Figure 1. This is accomplished with combined TD-DFT and coupled cluster methods [3], which are found to predict photochemical quantities with mean absolute deviations of 5-7 kJ/mol in comparison to experimental data.

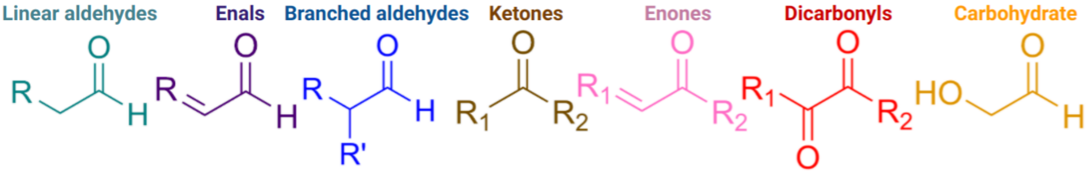

Figure 1: *SARs arising from carbonyl classes are computed for 20 representative species.*

Intrinsic barriers and photolysis thresholds are obtained, and energetic trends based on SARS are apparent, such as the propensity of α-bonds to break based on structural branching or conjugation. The data obtained are the quantities required for calculating theoretical photolysis rates, which could supplement photolysis parameters missing from atmospheric models, and provide a chemically rationalised framework to modify existing photolysis data to more appropriately model the diversity of carbonyls in the atmosphere.

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Using DFT and Semi-Empirical Methods as Alternative to QM/MM Approach to Study Biological Systems: Interaction between Metal Complexes Containing Phenanthroline Derivatives and DNA Duplex and G-quadruplexes.

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DFT and semi-empirical methods were used to study the interaction of two isomers of the $[Mo(\eta^3C_3H_5)Br(CO)_2(phen)]$ metal complex with DNA to gain insight on the comprehension and rationalization of its experimentally observed cytotoxicity [1]. Regular duplex chains of DNA and G-quadruplexes were considered to analyze several modes of interaction for the $[Mo(\eta^3C_3H_5)Br(CO)_2(phen)]$ metal complex. From a methodological point of view, the DFT treatment of the whole systems, ~500 atoms for the regular duplex DNA and ~1000 atoms for the G-quadruplex, including van der Waals contributions at the LMKLL/DZ2P level with the SIESTA software [2] gives excellent results at a reasonable computing time. PM6-DH2 [3,4] and PM7 [5] semi-empirical methods including also dispersion perform quite well for the geometries but the energetics of the system are not correctly described. From a biophysical point of view the $[Mo(\eta^3C_3H_5)Br(CO)_2(phen)]$ metal complex prefers the intercalation rather than the groove binding in the case of the regular DNA duplex, whereas for the G-quadruplex a system in which the $[Mo(\eta^3C_3H_5)Br(CO)_2(phen)]$ is totally inside the G-quadruplex is the most stable. Energy Decomposition Analysis and topological studies were also carried out to know the nature of the interaction and our results confirm the importance of the role of weak interactions. The cytotoxicity of $[Mo(\eta^3C_3H_5)Br(CO)_2(phen)]$ seem to be related to a subtle balance between the stabilizing weak interactions and the destabilizing steric contribution. The entropic factor associated to the solvation effects results also of great importance.

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Machine Learning Kohn-Sham Density Functionals from Molecules

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Kohn-Sham density functional theory (DFT) [1] is widely used to simulate electronic structures of materials owing to the balanced computational cost and accuracy. Accuracy of the DFT depends critically on the accuracy of its approximated exchange-correlation functional. Conventional strategies to construct functionals are, however, consist of complicated and heuristic combination of physical conditions, leading to difficulty in systematic improvement of their accuracy. Also, available physical conditions are often insufficient to determine the intrinsically complicated structure of functional. In order to overcome those difficulties and establish systematic way to improve DFT, we present a new strategy to construct a functional, which is not relying on the complicated use of physical conditions: application of the machine-learning (ML) scheme.

Here, Neural-Network (NN), which is flexible ML model with a large number of parameters, forms the functional structure. Recently, the NN has successfully constructed the exchange-correlation functional for a model system [2]. We demonstrate NN-based constructions of functionals for real materials within several semi-local approximation, including local spin density approximation (LSDA), generalized gradient approximation (GGA), and meta-GGA (Fig. 1) [3]. The NNs in those functionals are optimized (trained) to reproduce training data, composed of densities and energies of a few molecules obtained by accurate wave-function theories such as the coupled cluster method.

The trained NN-based functionals show comparable accuracies to existing functionals, even for hundreds of molecules which are not included in the training database. Also, with the same ML procedure, we have successfully constructed a non-local functional, which is conventionally difficult to construct due to lack of physical conditions. Those results imply that our ML scheme is effective to overcome existing problems in DFT, with utilizing the advantages of the data-dependent functional construction.

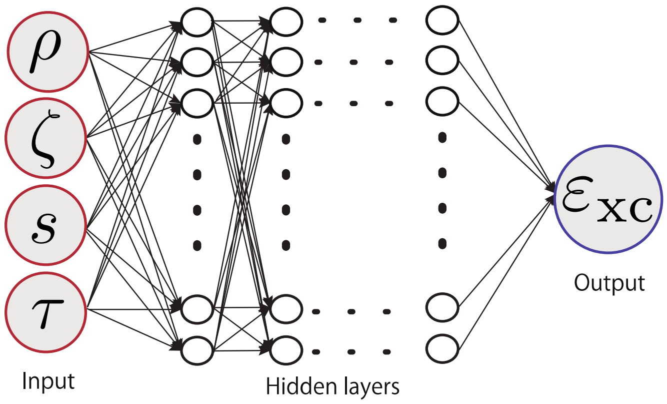

Figure 1: Structure of NN-based meta-GGA functional.

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Extension of the Optimal Control Theory to Solvated Systems

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Optimal control is a quantum theory designed to selectively guide a (molecular) quantum system from an initial state towards a final target state with desired properties (e. g. a given pure excited state), through the interaction of the system with an external laser pulse.

Many efforts have been devoted to the control of nuclear dynamics, allowing to successfully control products ratios of chemical reactions and crystallization processes, photodissociation of molecules in the gas phase, energy flow optimization in light-harvesting complex, and generally proving the method valuable in the conception of effective experiments .

Optimal control theory is widely applied to the study of molecular electronic states with ultrashort laser pulses, which require a short time scale (fs) to avoid nuclear relaxation and energy level rearrangements; with the application of optimal control theory it is possible to compute perfectly suited laser fields able to drive the system to the desired target state. Once the final shape of the pulse is obtained, the analysis of its polarization and frequencies can allow to understand the molecular behaviour and excitation mechanism.

Optimal control theory has been widely applied to in vacuo systems, but only few studies tried to include environmental effects into the calculations (e. g. dissipative coupling with the external bath, molecular geometry fluctuations). Nevertheless, none of them accounted for the modification in the molecular electronic and optical properties due to the dielectric nature of the solvent.

Electronic and optical properties of a molecule embedded in solution (or more generally, in a polarizable environment) can differ substantially from the ones of the same molecule in vacuo, therefore the optimal control of a solvated molecule needs a special consideration.

Electonic dynamics for a molecule in solution is coupled with the dynamics of the surrounding polarizable environment, i.e. the solvent. The Polarizable Continuum Model (PCM) provides a reliable description of the solvent dielectric properties, including polarization effects [1, 2]

Concerning optimal control pulses, two effects influences the optimal driving field: first, the presence of the molecule induces a polarization in the solvent (the reaction field) which influences the molecule itself; second, the effective field acting on the molecule is different from the external applied field, which in fact induces a further polarization of the environment (the so called cavity field effect) [3, 4].

Both these effects must be included in the Hamiltonian describing the system when deriving the optimal control problem for a molecule immersed in a solvent.

In this study we developed an optimal control theory for a molecule in solution subject to ultrashort laser pulses and applied it to quinolone and LiCN molecules, to understand how the effect of the solvent modifies the optimal control process itself.

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Calculating high precision, two-electron correlation data

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The aim of our work is to calculate high-accuracy two-electron correlation data using fully correlated and Hartree Fock methodologies implemented using in-house code[1], where higher than hardware double precision is essential. Although it is possible to calculate high precision data using computer algebra software, such as Maple, this comes with a substantial computational overhead. Numerically demanding linear algebra is preferred in C or C++, which requires libraries such as MPFR for arbitrary precision.

Recently, we have implemented ball arithmetic[2] for calculating two-electron integrals and Hartree Fock energies; which shows promising potential for quantum chemistry. It is shown that ball arithmetic provides rigorous error bounds for two-electron integrals and Hartree Fock energies where arbitrary precision data types suffer substantial and unpredictable error accumulation. Additionally DoubleDouble and QuadDouble data types[3] are employed within the fully correlated method to solve both sparse and dense linear systems providing high accuracy whilst minimising computational overhead. The fully correlated and Hartree Fock data provided using these in-house codes are used to calculate high accuracy correlation energies and Coulomb holes for heliogenic systems[4].

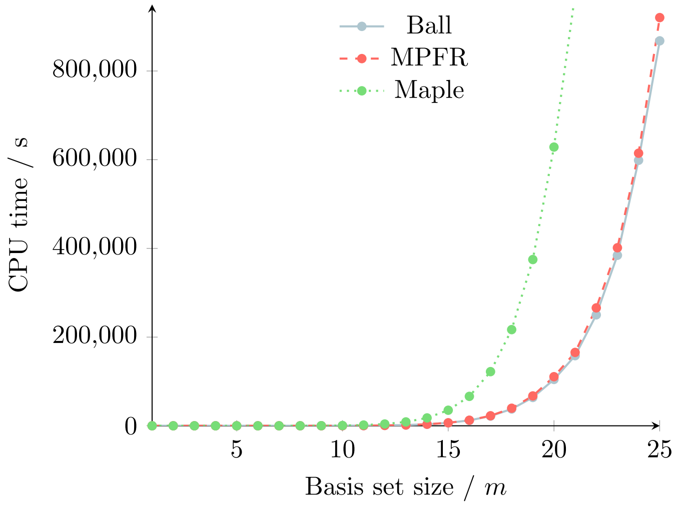

Figure 1: CPU time to calculate two-electron integrals at 200-digit precision using Ball arithmetic, MPFR and Maple.

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Charge-Transfer Surface Enhanced Resonance Raman: Effective Factor in Understanding the Selection-rules

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Surface-enhanced resonance Raman (SERS) is a powerful technique for ultrasensitive analysis and single-molecule detection. Since the discovery of SERS, elucidating the origin and selection rules of peak enhancements are the challenging and controversial process.[1] Different experimental and theoretical groups have tried to propose the unified model for variation of signal based on the two main mechanisms, electromagnetic (EM) and charge-transfer (CT) chemical.[2] The charge-transfer mechanism is associated with the resonance of the incident light with the CT states and plays a crucial role on the relative intensity and pattern of spectra. In our previous work,[3-5] the validity of time-dependent excited-state gradient approximation[6] to calculate the SERS-CT spectra of pyridine that adsorbed on the metal clusters has been demonstrated (in comparison to the experiment), and the controlling effects of ground-state and excited-state on the pattern of spectra has been justified. As the SERS intensity depends on the factors that modify the Raman tensors of different modes and the local fields polarization at the molecules, herein, we try to investigate the effect of adsorption site, molecular symmetry and orientation, and also the direction and amount of finite field on the pattern of SERS-CT spectra. We try to extend such an interpretation as a promising investigation that satisfactorily explain the experiment and propose the selection-rules for SERS-CT.

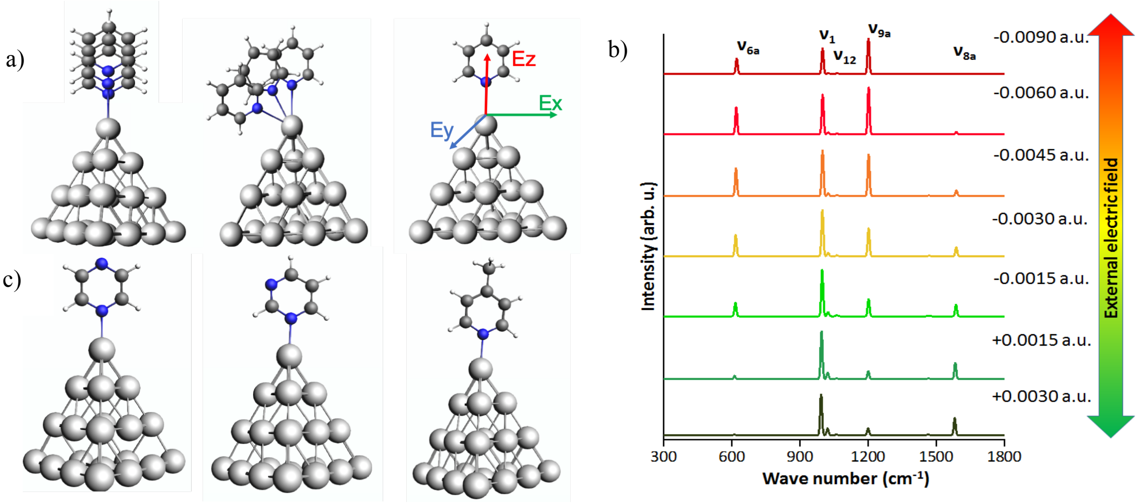

Figure 1: a) Chaning the oreintation of molecule and direction of applied field for Pyridine–Ag_{20}, b) SERS-CT spectra under the effect of external electic fields, c) benzenlike molecules with diffrenent symmtry adsorbed on Ag_{20}.

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A unified lattice model and modern statistical methods implemented in Surface Science Modeling and Simulation Toolkit

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Self-assembly of molecular monolayers on solid surfaces has a great potential for mass production of nanodevices and new materials. The development of experimental techniques, such as atomic-resolution microscopy, made it possible to see a huge amount of ordered structures formed by adsorbed molecules. Nowadays, the attention of researchers is focused on the development of processes for controllable self-assembly of nanostructures with desired properties [1,2]. It requires special theoretical tools that allow to predict *in silico* the self-assembly and properties of the monolayers. The time scale of self-assembly processes often significantly exceeds the typical time integration step in classical molecular dynamics. Thus, it is very difficult to obtain a representative sample even with the advanced sampling techniques.

To simulate complex adsorption systems, we propose the Surface Science Modeling and Simulation Toolkit (SuSMoST). It includes a number of utilities and implementations of statistical physics algorithms that allow to predict or explain the structure and thermodynamic properties of adsorbed monolayers. SuSMOST automatically builds formal graph and tensor-network models from atomic description of adsorption complexes. It aids *ab initio* calculations of interactions between adsorbed species. With methods of various nature SuSMoST generates representative samples of adsorption layers and computes its thermodynamic quantities such as free energy, adsorption layer coverage and density, heat capacity, entropy.

This study was supported by the Russian Science Foundation under Grant No. 17-71-20053.

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Theoretical Examination of Covalency in Berkelium(IV) Carbonate Complexes

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Elucidating covalency in actinides is gaining attention among the scientific community mainly due to fundamental chemistry aspects but also for separation chemistry purposes. Although covalency is not the main contributor to the chemical bond, it has been demonstrated that small differences in bonding may allow lanthanide/actinide or actinide/actinide separations. The strong complexation of oxygen-donor ligands such as the carbonate ion predominantly stabilizes Bk(IV) over Bk(III). Herein we propose two models of structures present in Bk(IV) aqueous carbonate solutions based on comparisons with experimental data previously reported for Bk(IV) carbonate solutions. Modeling further coordination of Bk(IV) in more basic concentrated carbonate solutions by addition of hydroxyl ligands, modifies the charge transfer spectral band with a second peak appearing toward longer wavelengths, that has also been observed experimentally. The multiconfigurational character of the ground and low-lying excited states is also shown along with strong spin-orbit coupling. Thus, the bonding properties of berkelium(IV) carbonate and carbonate-hydroxyl complexes are dominated by strong Coulombic forces where a non-negligible covalent character is confirmed by NBO analysis and topological studies of the electron density. Bond orders based in natural localized molecular orbitals (NLMOs) show that Bk–OH bonds present enhanced orbital overlap that is reflected in the bond strength.

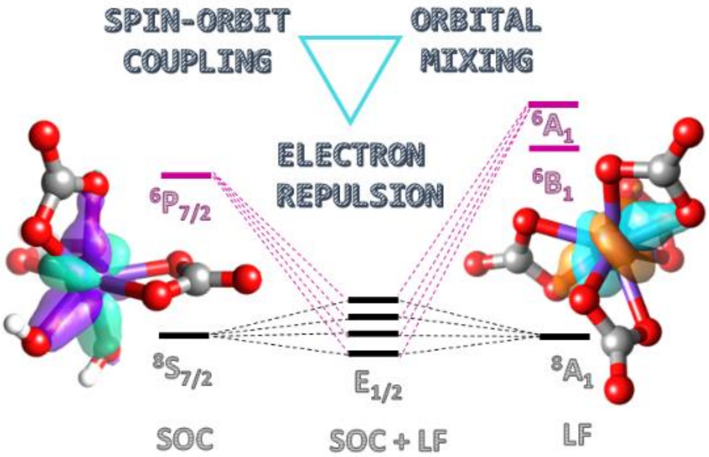

Figure 1: Bk(IV) carbonates are a good example of the interplay of spin-orbit coupling, electron repulsion, and covalency through orbital mixing in heavy elements.

Towards the H/D isotope effect
Size of benzene vs perdeuterated benzene

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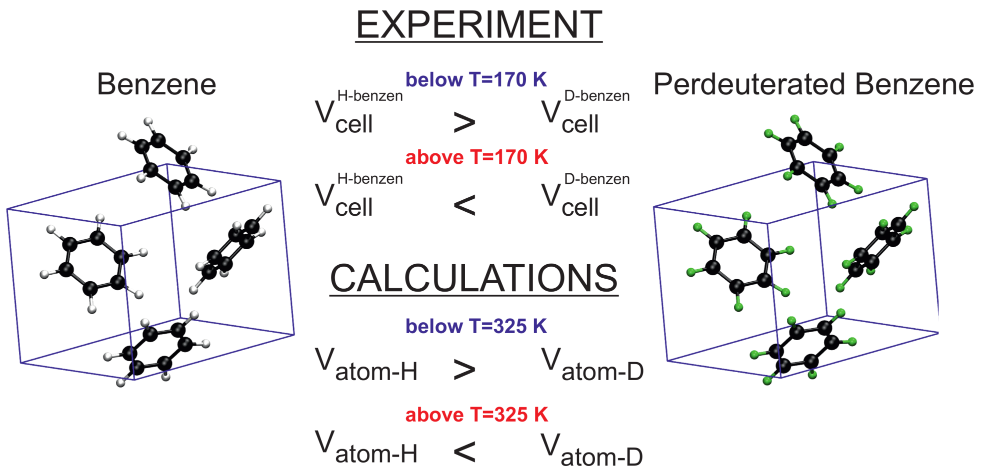
For crystalline systems isotope effect is manifested through different temperature expansion of unit cell volume of crystals containing distinct isotopes of the same element, as has been observed for benzene crystal and its perdeuterated counterpart. [1] The differences in temperature expansion of the cell are commonly attributed to changes of atomic effective sizes of isotopes due to atomic masses.

We propose to employ an innovative procedure [2] to determine the effective atomic sizes, based on three-steep routine in which the problem of finding an effective size of each atom is reduced to determination of volume inside which atom can be find with suitably high probability.

Our procedure is repeated for *ab initio* trajectories [3,4] computed with different target temperatures for benzene and perdeuterated benzene crystal and enables us to study temperature-driven changes of the effective size of H and D atoms.



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Grand canonical Monte Carlo simulation of Fe-terephtalate ordering on Cu(100)

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Surface confined metal-organic networks (SMON) have been attracting much attention in recent years, since they represent a unique type of two-dimensional materials that have new magnetic, electronic and catalytic properties [1,2]. The structure of SMONs is similar to the metalloenzymes. Therefore, it can be also considered as models to study the chemical reactivity in living matter [3]. SMON structure is determined by a subtle balance between molecule-molecule interactions, metal-molecule interactions, and molecule-surface interactions. In this regard, the structure and properties of SMON are much richer comparing to 3D MOFs. For the same reason, the structure and physicochemical properties of SMON are extremely difficult to control. It requires a detailed understanding of the mechanisms and driving forces of the SMON self-assembly.

Here we report a detailed lattice model of terephthalic acid (TPA) and iron ordering on Cu (100) surface under ultra-high vacuum conditions, taking into account multiple interactions in the adlayer: carboxylate-Fe coordination, hydrogen bonding and surface mediated interactions. We have calculated the phase diagram of the adlayer using the ground state analysis and grand canonical Monte Carlo simulation as implemented in the SUSMOST code [4]. It has been established that one type of the ladder structures distinguished on scanning tunneling microscopy images is a metastable state and not a phase in the thermodynamic sense. We have found two new metal-organic structures, which are missed in earlier studies, but apparently formed in the TPA-Fe/Cu(100) adsorption layer. The first one is characterized by the lowest density of the monolayer. Another phase is formed at high densities, even higher than the densest structure observed experimentally.

Also we have revealed that long-range interactions between Fe-Fe and TPA-Fe are needed to reproduce most of the structures found experimentally [2].

We believe that our theoretical investigation insights will be helpful for understanding the self-assembly of metal-organic networks on metal surfaces and stimulate further experimental work.

This project is supported by the Russian Science Foundation (Grant No. 17-71-20053).

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On Camptothecin Aggregation in DMSO and Aqueous Solutions

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The lactone form of quinolone alkaloid camptothecin (CPT), (S)-4-ethyl-4-hydroxy-1h-pyrano[3‘,4‘:6,7]-indolizino-[1,2-b]-quinoline-3,14-(4h,12h)-dione, is a potent anticancer drug (Fig. 1). The shifts of its two strong peaks in a critical 300-400 nm region of UV-Vis absorption spectra in neutral DMSO and aqueous solutions of various CPT concentrations may be explained by the formation of J-aggregates with bathochromic shift in absorption bands. These are formed by the stacking interaction between quinoline rings of CPT chromophores with the inverse position of the nitrogen atoms [1, 2]. Dvoranova *et al.* [2] investigated UV–Vis absorption spectrum of 50 μM CPT in various solutions. They performed B97D/cc-pVDZ geometry optimizations of the CPT lactone monomer and of its head-to-tail π-dimer in six solvents treated within Integral Equation Formalism Polarizable Continuum Model (IEFPCM). Unfortunately, the difference between the TD-B3LYP calculated electron transitions (1 – 5 nm) was very small in comparison with the difference between experimental bands (6 – 17 nm) in all the solvents under study. In the next study [3] the structures of CPT lactone head-to-tail π-aggregates in the *anti* conformation up to tetramers were optimized in DMSO and aqueous solutions using various DFT functionals with cc-pVDZ basis sets. Solvent effects were estimated using IEFPCM treatment. Only B3LYP with D2 dispersion correction of Grimme and ωB97XD functionals were able to produce reliable results on their geometries and TD-B3LYP electron transitions..

This study deals with the geometry optimization of CPT lactone head-to-tail π-aggregates in the *syn* conformation up to tetramers in DMSO and aqueous solutions using B3LYP with D2 dispersion correction of Grimme and ωB97XD functionals, cc-pVDZ basis sets and the IEFPCM approximation of solvent effects. Our results indicate that the *syn* conformation is more stable than the *anti* one but the agreement of its TD-B3LYP electron transitions with experimental spectra is worse.

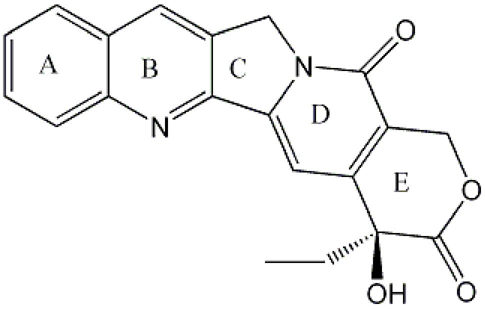

Figure 1: Molecular structure of CPT in the lactone form with standard ring notation.

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Understanding the aqueous speciation of molecular metal oxides

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The behavior of metal oxides clusters at aqueous solution is dictated by numerous complex and interrelated phenomena. The most important features of metal-oxo clusters in solution are well understood and predictable while others are confounding, interdependent and variable. It is well known how polyoxometalates (POMs) of Mo, V and W are assembled and behaving in solution. On the other hand, formation mechanisms of Nb and Ta POMs are not well understood and described. Thus, there is a lack of knowledge of how Nb and Ta POMs behave in solution and this information is needed to understand the structural evolution among different POMs.[1]

The decaniobate ion ($[Nb_{10}O_{28}]^{6-}$, Nb_{10}) is unique in solution as it does not strongly protonate when dissolved in water and is stable at near neutral pH. However, it converts to hexaniobate ion ($[Nb_6O_{19}]^{8-}$, Nb_6) with pH increase. It is know that the conversion from Nb_{10} to Nb_6 proceeds via heptaniobate ion ($[Nb_7O_{22}]^{9-}$, Nb_7), which is detectable by ^{17}O NMR spectroscopy and ESIMS.[2] (Figure 1)

In that sense, we have used Density Functional Theory (DFT) to rationalize the observed species in solution, and develop an understanding of the solutions behaviors, in order to find a plausible reaction mechanism for the base-induced dissociation of Nb_{10}. The results show how important is to use computational chemistry to rationalize the experimental observations.

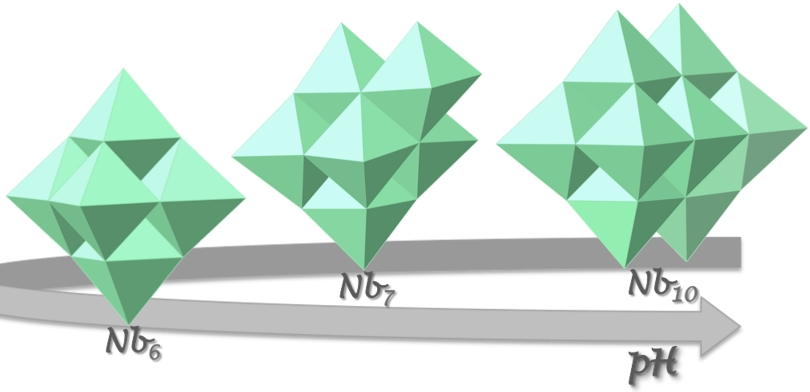

Figure 1: Representation of observed species in solution at different pH conditions.

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Theoretical view on atomic mobility in rare gas matrices

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There is a lot of experimental studies indicating the activation of the matrix-isolated atoms at distinct and sharp temperature thresholds. The most are observed for light atoms, such as hydrogen, nitrogen, oxygen, etc., though some observations suggest that the same phenomena also occur for heavier atoms including the d-elements. Theoretical attempts to describe tempearture-activate migrations had also been going on for a long time, but the complexity of the problem prevented the simple models to reach even qualiative agreement with the experimental data.

In this work, we describe more sophisticated approach for theoretical investigation of the mobility of hydrogen and oxygen atoms in argon, krypton and xenon matrices. It relies on the the previously proposed method for determining the stable atomic trapping sites in inert gas crystals [1,2], the molecular-mechanical approach and accurate non-empirical data for the diatomic systems. Using this approach, we study the A@RG systems (A = H, O, RG = Ar, Kr, Xe) with the different numbers of RG atoms removed from the lattice to find their equilibrium geometries and energies. Using the thermodynamic concept of the convex shells, we determine what trapping sites are thermodynamically stable. The number of stable trapping sites found for each atom in each matrix is fully consistent with the available experimental data and with generic theoretical prediction [3] at the given parameters of the diatomic interaction potentials. In the case of atomic hydrogen, the results are also verified against the electron spin resonance data. The numerical estimations of the shifts of the hyperfine structure constant are obtained assuming the additivity of the Fermi contact interactions. The dependences of the isotropic components of the hyperfine structure constant and the g-tensor on the H-RG systems distance are calculated *ab initio.* The additive approximation is tested for the first coordination polyhedron by the direct *ab initio* calculations for the HRG_n subsystems.

Possible migration paths between the stable trapping sites found, as well as between crystal vacancies, are investigated using the nudged elastic band technique and then refined by the intrinsic reaction coordinate method. The barriers found for both H and O atoms are in good correspondence with the measured the confirming different migration mechanisms and pathways proposed theoretically.

We thank Daniil Izmodenov and Iosif Leibin for their contribution and the Russian Science Foundation for financial support under the project #17-13-01466. Part of calculation was carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

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Non-Born-Oppenheimer Electronic-Vibrational Structure Applied to Vibronic Spectra Prediction

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The Born-Oppenheimer (BO) potential energy surface has been a central quantity in the understanding of chemical dynamics for over 80 years, allowing the adiabatic separation of electronic and nuclear degrees of freedom. The breakdown of the BO approximation occurs in many chemically important circumstances, with many current difficulties arising from the coupling of many nuclear degrees of freedom within a potential energy surface.

By employing harmonic approximations to vibrational degrees of freedom and linear electronic-vibrational couplings, we treat electronic and vibrational degrees of freedom quantum mechanically and simultaneously.

We apply these approximations to both model and chemical Hamiltonians to efficiently predict gas phase vibronic spectra and condensed phase optical spectra using time-dependent mean-field theory.

Rational co-catalyst design for amide hydrogenolysis based on DFT calculations.

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The reduction of electron rich carboxylic acid derivatives, such as amides, is still a difficult reaction. In a recently reported method, amide hydrogenolysis was enhanced by the combination of a secondary amide co-catalyst with $(^{iPr}PNP)Fe(H)(CO)$ (^{iPr}PNP = $N[CH_2CH_2(P^iPr_2)]_2$).[1] The mechanism for this reaction was studied in our group by using DFT methods.[2] The M06 functional was selected based on a method benchmark using CCSD(T). The mechanistic study showed that the secondary amide co-catalyst acts as a proton shuttle in the rate limiting step ($\Delta G^{\ddagger}_{HT}$) but poisons the catalyst forming an adduct (ΔG_{add}) (Figure 1). In order to improve this reaction, ΔG_{add} and $\Delta G^{\ddagger}_{HT}$ were calculated using as co-catalysts the molecules shown in Figure 1 and then introduced in a microkinetic model to predict the expected amide conversion.[3] The most promising candidates were tested in the lab and the experimental results were in good agreement with the computational predictions. Co-catalyst 1 yielded the highest conversion, owing to an optimal balance between ΔG_{add} and $\Delta G^{\ddagger}_{HT}$.

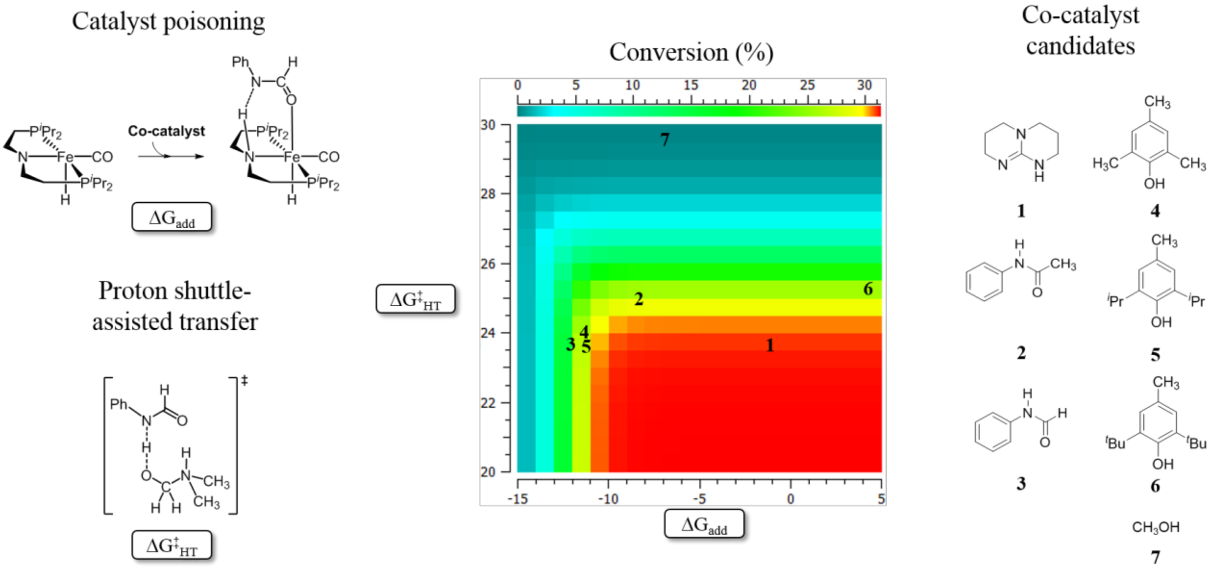

Figure 1: Key reactions in the amide hydrogenolysis co-catalyst design (left); predicted conversion vs ΔG_{add} and $\Delta G^{\ddagger}_{HT}$ (middle); co-catalysts tested (right).

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Topology-Driven Molecular Electronics Lacking π-Conjugation

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Is π-conjugation necessary to achieve efficient transport in molecular electronics? In this work we use Non-Equilibrium Green's Functions technique coupled with Density Functional Theory to demonstrate how molecular topology can be used to boost the tunneling transport in single-molecule junctions featuring saturated hydrocarbon bridges.[1] Specifically, caged saturated hydrocarbons offering multiple σ-conductance channels afford transmission far beyond what could be expected based upon conventional superposition laws, particularly if these pathways are composed entirely from quaternary carbon atoms. Computed conductance of molecular bridges based on carbon nanothreads, *e.g.*, polytwistane, is not only of appreciable magnitude; it also shows a very slow decay with increasing nanogap, similarly to π-conjugated wires (Figure 1).

Conventional approaches to highly conductive single-molecule junctions involve π-conjugated systems with appropriately tuned energy levels of the frontier molecular orbitals. Our findings put forward an alternative strategy for modulating the transport in unimolecular electronics that is based on molecular topology and succeeds even in systems completely lacking π-conjugation, e.g., carbon nanothreads, diamondoids and graphane derivatives.

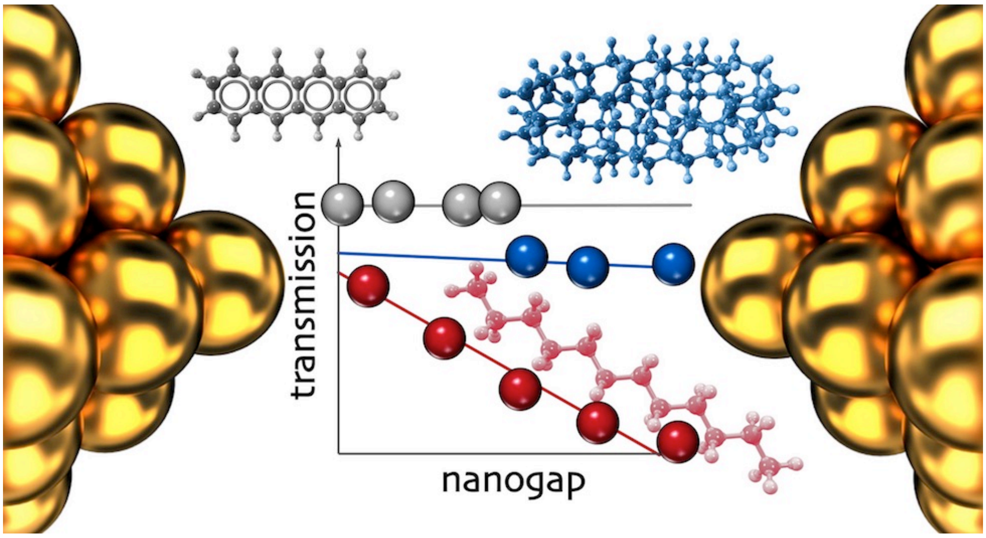

Figure 1. Computed junction transmissions *vs.* increasing molecular lengths.

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Without Compromising Efficiency and Accuracy: Solving the Nuclear Schrödinger Equation using Path Integral Monte Carlo Simulation with Modified Shepard Interpolation

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Feynman's path integral formalism describes nuclei in a quantum system as "ring polymers", which describe the closed quantum paths the system can take. Thermodynamic properties, described in terms of the thermal density matrix, are calculated by sampling all possible paths using Monte Carlo simulation, which are weighted by their action. The convergence of the method, that is, the number of beads for each ring polymer and the number of Monte Carlo steps taken, can be improved by using more accurate description of the action (Symplectic schemes). We compare the convergence efficiency between four current existing action formalisms, primitive approximation (PA), Takahashi-Imada (TI), Suzuki factorisation (SF), and Chin approximation (CA) formalisms. [3] We further numerically optimised the parameters for SF and CA schemes, by doing so, lower order commutators roughly cancel in order to achieve higher order numerical accuracy and improve the computational efficiency. We apply the resulting schemes to three realistic systems, H2O,[1] HCN-HNC, [2] and CH4. The first two systems adopted relatively inexpensive however spectroscopically accurate PESs in order to demonstrate the convergence efficiency between four formalisms. The PES of methane was constructed by using modified Shepard interpolation, [4] that is, as a weighted sum of second order Taylor expansion about a set of PES data points at regions of interest, calculated at a given level of electronic structure theory, the technique for combining modified Shepard interpolation and path integrals formalisms is novel, and we intend to demonstrate that it is efficient and potentially accurate to calculate the total internal energy for systems larger than four atoms.

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GW(Γ) calculation for photoabsorption energies of spin polarized systems

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There has been an increasing demand of using the GW method[1] based on many-body perturbation theory not only in the field of solid-state physics but also in the field of quantum chemistry, and many codes installing this method have been developed recently. However, the usual GW method enables one to calculate photoemission and inverse photoemission spectra (PES/IPES) only. To calculate photoabsorption energies (PAEs), one had to additionally solve the Bethe–Salpeter equation (BSE). Since this method combines the GW calculation and the BSE calculation, this method is called GW +BSE method[2]. This method should deal with not only the one-particle Green's function in the GW part but also the two-particle (electron-hole) Green's function in the BSE part, and doubly induces the evaluation errors. It has been recently reported that the GW + BSE method significantly underestimates the experimental PAEs of small molecules[3]. To avoid these problems, it is highly desirable to develop a new GW method to calculate PAE without solving the BSE. The idea is very simple: Just to use the pure GW method to the cationic systems not to the neutral systems. Then, one may obtain the PAE from the quasiparticle (QP) energy differences between the (one electron missing) hole level and the higher empty levels. It enables one to identify the rigorous one-to-one correspondence between the PAE peak and the ("extended") QP level. This simple idea yields the PAE with a reasonable accuracy. This method is particularly useful for radical systems but is applicable for both closed shell and open shell atoms and molecules. We applied the self-consistent LGWΓ[4] method including the vertex correction to our method. Figure 1 shows the absolute difference between the calculated and experimental values of the first photoabsorption energy. As seen in Figure 1, this method gives PAEs within 0.1 eV accuracy.

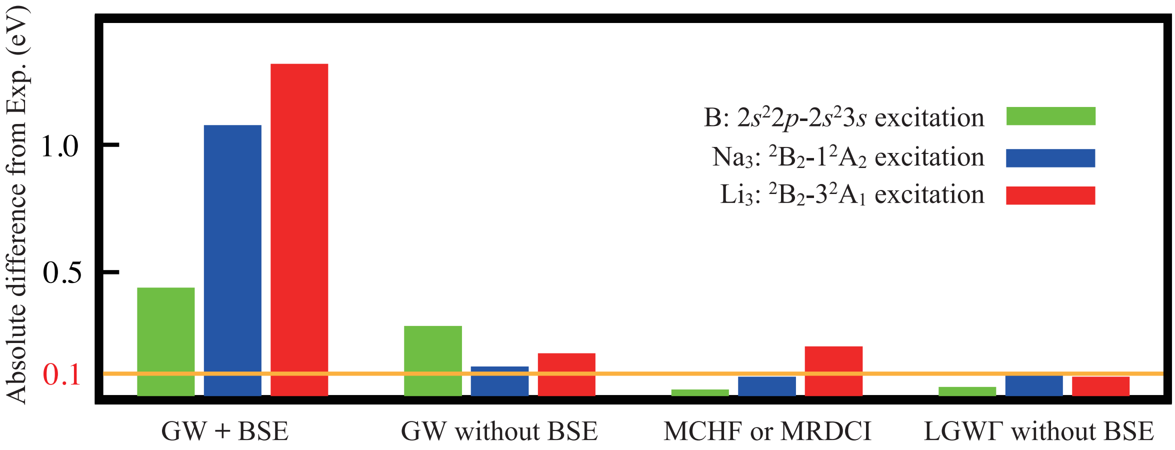

Figure 1: First photoabsorption energies of B, Na$_3$, and Li$_3$[5]

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Accelerated molecular dynamics simulation of glutamine recognition and binding by γ-glutamyltransferase.

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The enzyme-substrate molecular recognition process is a complex sequence of events which takes place on the microseconds to seconds time scale, thus its simulation requires the use of enhanced sampling methods to speed up phase space exploration. In particular, accelerated molecular dynamics (aMD) works by flattening the molecular potential energy surface, adding a non-negative boost potential when the system potential is lower than a reference energy [1]. We applied aMD to the study glutamine recognition and binding by γ-glutamyltransferase (GGT) [2]. Our approach allowed us to model the process of substrate recruiting by the enzyme and to identify a four step pathway describing the approach to GGT of a glutamine molecule, from the free state to its full insertion into the active site. In the first step (Fig. 1a), glutamine approaches the binding pocket without directly interacting with the inner residues and it is still able to depart from the protein surface. In the second step, glutamine orientation allows the formation of a stabilizing interaction between the negative charge on the carboxyl group and the N-terminus of Thr$_{391}$. Glutamine's amino group is also oriented towards a negatively charged pocket formed by Asn$_{411}$ and Asp$_{433}$ (Fig. 1b). In the third step of the proposed recognition pathway, the interaction established between glutamine amino group and Asn$_{411}$ and Asp$_{433}$ is associated to the weakening of the interaction between glutamine carboxyl group and Thr$_{391}$. This drives glutamine deeper into the binding pocket (Fig. 1c). Finally, in the fourth step glutamine attains its final binding pose into the catalytic site. The carboxyl group forms a salt bridge with Arg$_{114}$, the amino group is stabilized by the aforementioned negative pocket and the amidic group is now close to the hydroxyl oxygen on Thr$_{391}$, ready to react.

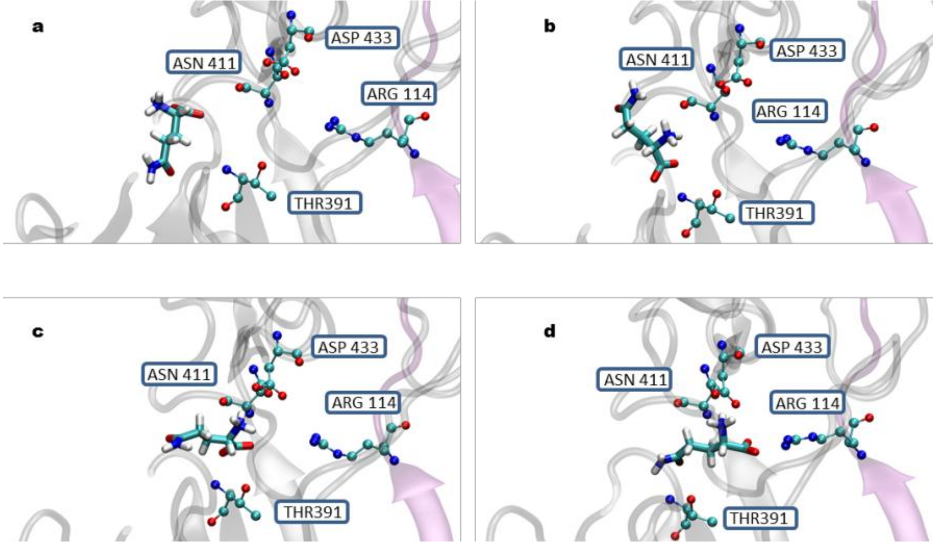

Figure 1: The four steps of our proposed binding pathway. Glutamine is represented in licorice, relevant GGT residues in CPK.

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Computational investigation on photonics of boron and zinc dipyrromethene complexes

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The last decades were characterized by increased interest in the development of various optical devices based on complex molecular compounds. Depending on the structure, they are widely used including active laser media of tunable lasers, laser limiters, fluorescent tags, optical sensors in various fields of science and technology [1]. Currently, dipyrromethenes with p- and d- elements are the most promising compounds to apply as elements of these devices. The most perspective members of this family are boron fluorinated complexes of dipyrromethenes (BODIPY). BODIPYs possess intense fluorescence in the visible range and good photostability. Dipyrromethenes can form stable complexes with ions of d-elements such as Zn(II). In comparison with BODIPY, an advantage of complexes of d-metals with dipyrromethenes is high sensitivity of the photonics characteristics to changes in the chromophore structure and nature of the solvent as well as easier "self-assembly" of these complexes. It makes them very promising for fluorescent probes dipyrromethenates have efficient absorption and emission in the visible spectral region and they are sensitive to structural changes in their molecular environment.

New derivatives are been synthesizing with increasing intensity but at the same time theoretical researches of their physical and chemical properties to develop optical devices is going essentially slower. Experimental investigation complemented with theoretical-computational studies accompaniment lead to deeper understanding of electronic structure, pathways of electronic transitions, and specific spectral-luminescence features to develop more efficient fluorescent probes, optical sensors and triplet photosensitizers. Therefore, the purpose of the present work is theoretical research of photophysical and photochemical processes occurring in dipyrromethenes molecules and depending on their structure, nature of the solvent and the characteristics of the exciting radiation.

In order to optimize the compounds in ground and excited states as well as to investigate their electronic structures, schemes of excited energy dissipation, several TD-DFT functionals accompanied with various basis sets were used. Two CH_3-BODIPY absorption bands in the experiment with λmax = 504 nm (ε = 84000) and 350 nm (ε = 4200) were in agreement with calculated wavelengths of 476 nm (ε = 24678) and 397 nm (ε = 1204), respectively, where as the experimental $[Zn(dpm)_2]$ bands with λmax = 485 nm (ε = 146200) and 346 nm (ε = 9750) were at 457 nm (ε = 260000) and 403 nm (ε = 32400) in calculations [2]. The calculated wavelengths are in satisfactory agreement with the experimental ones (the difference is about 30 nm). The molar extinction coefficients differ, but their trends are correctly reproduced.

This research was supported by the State Task of Russian Ministry of Education and Science (project no. 4.6027.2017/8.9) and The Tomsk State University competitiveness improvement programme.

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Internal Oriented Electric Fields as a Strategy for Selectively Modifying Photochemical Reactivity

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Recent work[1] in our group has been focused on studying the effect of static electric fields on reaction kinetics and thermodynamics, and to what extent these effects are general and applicable. Up to now, however, the application of electric fields to electronic excited states has been largely confined to Stark spectroscopy, rather than as a usable strategy for deliberately altering excited states. Here, we present a proof-of-concept study[2] into the feasibility of applying static electric fields as a way of tuning photochemical behavior, using charged functional groups (acid/base groups) as the means by which the electric field is applied. We demonstrate that, with acetophenone, the electric field effects are large, usable, and persistent in high-polarity solvents.

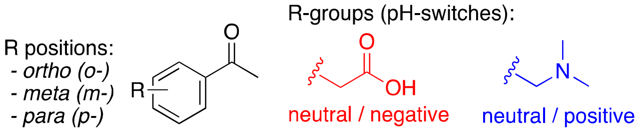

Figure 1. CFG-functionalized acetophenone

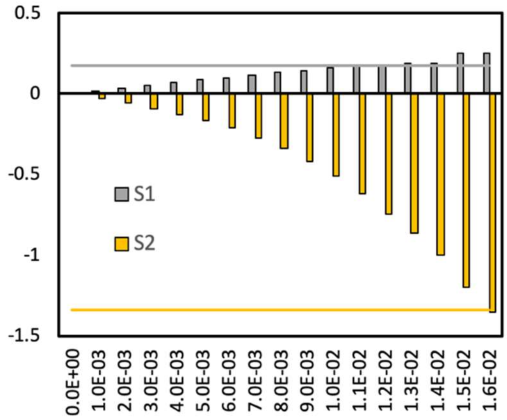

Figure 2. Change in $^1n\pi^*$ and $^1\pi\pi^*$ vertical excitation energies on uncharged, m-carboxy functionalised acetophenone with increasing static electric field strength

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Uncertainty estimation for exploring chemical space with neural networks

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Machine learning has enormous potential to accelerate material discovery by supplementing first-principles density functional theory (DFT) simulation with low-cost approximations from artificial neural networks (ANNs). This allows many more configurations to be explored than would be possible using DFT alone, and is particularly valuable where existing knowledge is limited and simulations are expensive and challenging, such as in the design of transition metal (TM) complexes, which have important applications as selective homogeneous catalysts and molecular sensors.

However, even models that show good performance on test data can fail to generalize when used to explore diverse chemical space because training data invariably reflects the biases and limitations of the data generation process, often being restrictive in chemical variety or focusing on already well-explored chemical space, e.g. small organic molecules. These problems are exacerbated for TM complexes where large databases are not available and understanding of similarity is less established. If ML models are to realize their potential for discovery, they must be equipped with reliable measures of system-specific uncertainty. We previously introduced a simple heuristic based on distance to training data in feature space that correlated well with model uncertainty, and we used it to design spin crossover materials and complexes with targeted frontier orbital properties from diverse pools of candidates using a genetic algorithm. Because we could control model uncertainty, a majority of our leads were validated using DFT.

Unfortunately, such geometric estimates are dependent on good feature engineering and are not straightforwardly applicable in cases with large feature vectors or when using deep networks to learn from simple representations, e.g. graph convolutions. Instead, we propose measuring similarity in the ANN latent space, which provides substantial improvements over raw feature distances. We convert distances into quantitative uncertainty metrics using a simple probabilistic model, and compare to commonly-utilized uncertainty metrics for ANNs: ensemble models and Monte Carlo dropout, in two applications 1) generalization of spin splitting energy predictions trained on simple ligands to experimental structures from the Cambridge Structural Database and 2) atomization energy predictions on a benchmark organic data set. We observe that the proposed model provides the best performance, without requiring additional investment in training multiple models. This makes the proposed model an attractive candidate for active learning and chemical discovery.

Theoretical investigation in preparing water-soluble $Au_{25-n}M_n$ (M = Au, Ag, Cu, Pd, Pt) Nanoclusters with atomic precision

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Ultrasmall (< 2 nm), water-soluble noble metal nanoclusters have shown great potential in bio-imaging, diagnosis, and therapy for heavy ills (such as cancer, Parkinson's disease *etc*.). Benefiting from the small size, the atomic composition of these clusters has been well elucidated by ESI-MS, and EXAFS *etc*. Fantastic size effect was observed, that is, the physical-chemical properties and the physiologic functional of these nanoclusters are highly dependent on their atomic size (mainly the number of metal atoms). However, the precise atomic structure, and especially the metal-metal or metal-ligand binding modes of these clusters, have been rarely reported to date. The ambiguity in atomic structure remarkably limited the investigation on their structure-property correlations and the practical application.

In the regime of the "precision to precision" protocols[1,2], we herein used density functional theory (DFT) calculations to probe the thermodynamic plausibility and inherent determinants in synthesizing atomically precise, water-soluble clusters via the framework-maintained two-phase ligand exchange method. A series of rod-like $Au_{25-n}M_n$ (M = Au, Ag, Cu, Pd, Pt) clusters with the same framework but varied ligands and metal composition were chosen as the modeling reactants, and cysteine was used as the modeling water-soluble ligand (). It was found that the acidity of reaction conditions remarkably affect the thermodynamic facility of the ligand exchange reactions. Ligand effect (structural distortion and acidity) dominates the overall thermodynamic facility of the ligand exchange reaction, while the number and type of dopped metal atom(s) can only slightly adjust the reaction rates.

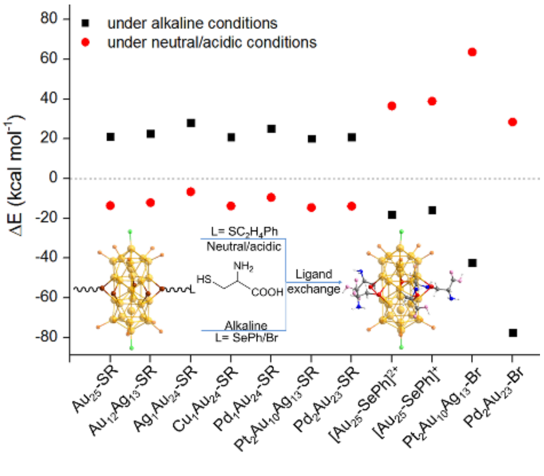

Figure 1: The framework-maintained ligand exchange of $Au_{25-n}M_n$ nanoclusters.

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Prediction for photophysical properties of thermally activated delayed fluorescent emitters and application to carbazole-oxadiazole derivatives

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Highly efficient thermally activated delayed fluorescent (TADF) emitters have significant attention in the field of organic light-emitting diodes (OLEDs) to develop high performance. TADF emitters allow the internal quantum efficiency (IQE) theoretically up to 100% by harvesting both singlet and triplet through the reverse intersystem crossing (RISC). Prediction of energy difference between first excited singlet state (S_1) and first excited triplet state (T_1), ΔE_{ST}, is important to design highly efficient TADF emitters because ΔE_{ST} is highly related to reverse intersystem crossing rate (k_{RISC}). Here, we developed methods to predict ΔE_{ST} based on time-dependent density functional theory (TD-DFT). Moreover, k_{RISC} was computed by Fermi Golden rule [1] and Marcus theory [2]. We found that k_{RISC} is correlated with decay time of TADF emitters. We applied our methods to carbazole-oxadiazole derivatives, and TADF devices made from carbazole-oxadiazole-based materials were shown to small ΔE_{ST} with high external quantum efficiency of up to 24.4% [3]. These results demonstrate that prediction of energy differences and k_{RISC} are promising methods and parameters for application in developing highly efficient TADF system.

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Understanding of binding molecular mechanism of hemagglutinin H3N2 of influenza virus complexed with arbidol and derivatives: A molecular dynamics simulation perspective

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Recently, the H3N2 influenza outbreak has caused the serious global public health concern for the next influenza pandemic control. Since using of current anti-influenza drugs targeting on neuraminidase (oseltamivir and zanamivir) and the proton M2 channel (amantadine and rimantadine) leads to drug resistance, it is essential to seek for new anti-viral agents that act on additional viral targets. Hemagglutinin, a glycoprotein embedded in the viral surface and playing a critical role in influenza viral replication cycle has become as attractive target. This work investigates the binding molecular mechanism of hemagglutinin H3N2 of influenza virus complexed with arbidol and its derivatives by means of molecular dynamics simulation. The result showed that arbidol derivatives could form strong hydrogen bonds with surrounding amino acids such as THR59 (HA2), ASP90 (HA2), LYS307 (HA2), GLU103 (HA2), LYS58 (HA2) and ASN60 (HA2), while arbidol is not able to make this kind of interaction. Moreover, the binding free energy prediction is in agreement with experimental data indicating that derivative compounds show high potency against hemagglutinin H3N2. Detailed information is very helpful for further design and optimize hemagglutinin inhibitors with high efficiency.

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Hybrid membranes of lipids and diblock copolymers : from homogeneity, raft, to phase separation[1]

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Hybrid lipid/polymer vesicles can integrate benefits of liposomes and polymersomes. In this work, the phase behavior of hybrid membranes containing lipids and diblock copolymers is explored by dissipative particle dynamics simulations. The influences of lipid unsaturation and thickness mismatch between lipids and polymers are considered. The transition from the mixing state (homogenous distribution) to demixing state (formation of bilayered lipid-rich domains) is always observed as the lipid concentration (φ_l) exceeds a critical value, which increases with the degree of unsaturation. It is found that phase separation is driven by weak energy incompatibility between the hydrophobic segments of lipids and polymers. When the effect of thickness mismatch becomes significant, the occurrence of the demixing state is retarded, and monolayer lipid rafts emerge before phase separation. Lipid fluidity associated with the physical state of a hybrid membrane can be characterized by lateral lipid diffusivity (D_l). In the polymer-rich membrane, D_l is higher in the mixing state, but decreases generally with φ_l due to lipid-lipid interactions and interdigitation.

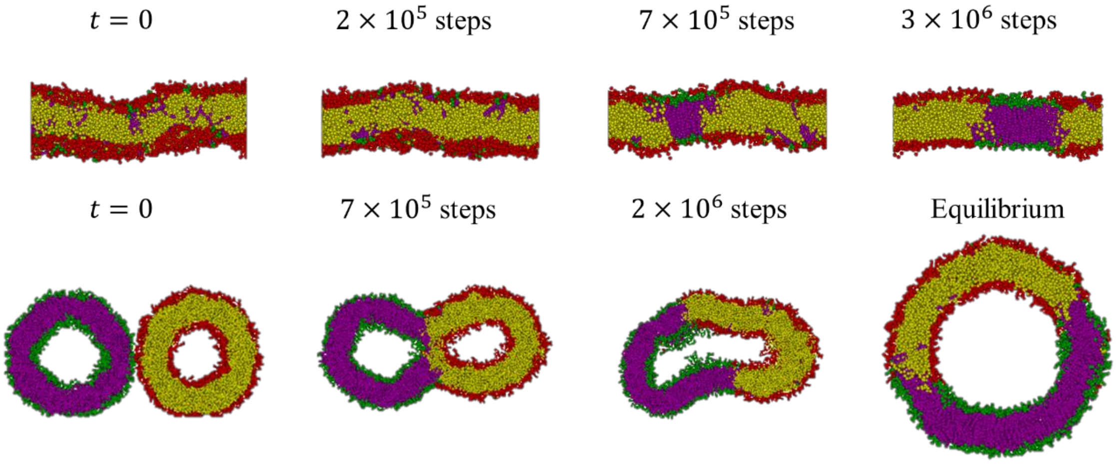

Figure 1: Time evolution of the development of phase separation in a hybrid bilayer membrane and a hybrid small unilamellar vesicle.

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A classical ride through a conical intersection

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Regarding the correlated electron-nuclear motion in a model system, we investigate the dynamics in the vicinity of a conical intersection (CoIn) between two excited state potential surfaces. It is documented that an ensemble of classical trajectories which move in the complete electronic-nuclear phase space tracks the quantum wave-packet motion through the CoIn which is accompanied by a strong non-adiabatic population transfer. On the contrary, for an adiabatic circular motion around the position of the CoIn, the quantum mechanical and classical densities deviate substantially. In the latter case, the Born-Oppenheimer classical nuclear motion on a single potential surface is able to track the quantum dynamics.

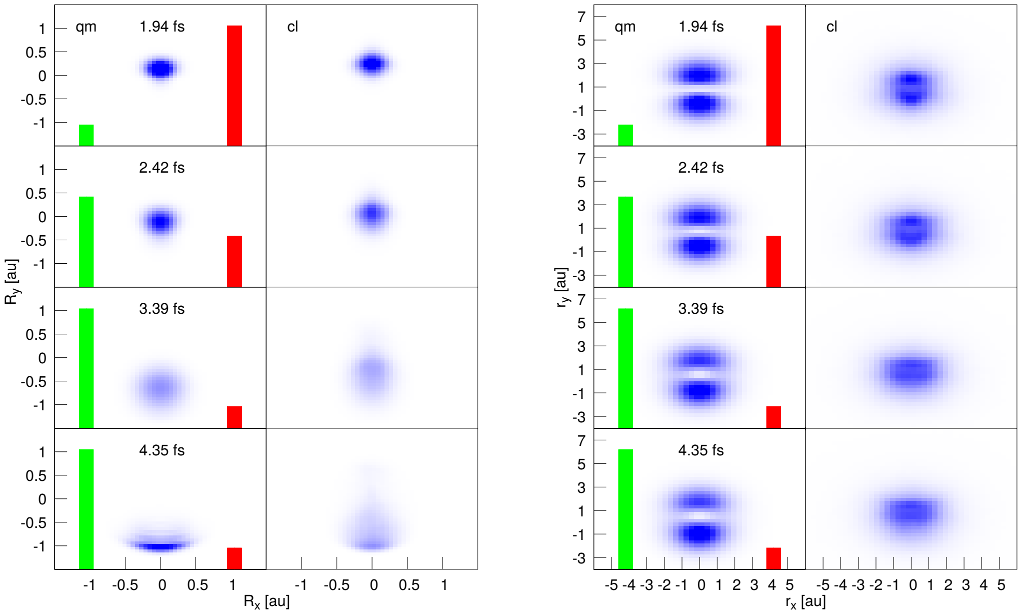

Figure 1: Quantum (qm) nuclear density, with its classical (cl) counterpart (left). Quantum electronic density and its classical counterpart (right). The bars show the population of the second (green) and first (red) excited state.

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Slowing and cooling of AlF molecules

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The realization of ultracold molecules is fundamental for the study of ultracold chemistry, for precision measurements to test fundamental symmetries and for quantum information and simulation. Most of the theoretical and experimental efforts have been devoted to bi-alkali molecules via photo-association of two ultracold atoms. However, ultracold molecules can also be produced by trapping and cooling molecules from a molecular beam. Here, we present a joint theoretical-experimental study about slowing and trapping of AlF down to temperatures $\sim 100\mu$K. In particular, the measured and available spectroscopy information for the $X^1\Sigma$, $a^3\Pi$ and $A^1\Pi$ electronic states is inverted to get the pertinent potentials, and realistic Franck-Condon factors. The results obtained are shown in Fig.1 and indicate that only a single re-pump laser will be required for the cooling of AlF. The Spectroscopy characterisation of the relevant ro-vibrational and electronic states allows us to explore the slowing of the molecules as a function of the detuning and intensity of the applied laser field, which is theoretically modelled by means of the optical Bloch equations between the 36 ground and 36 excited states.

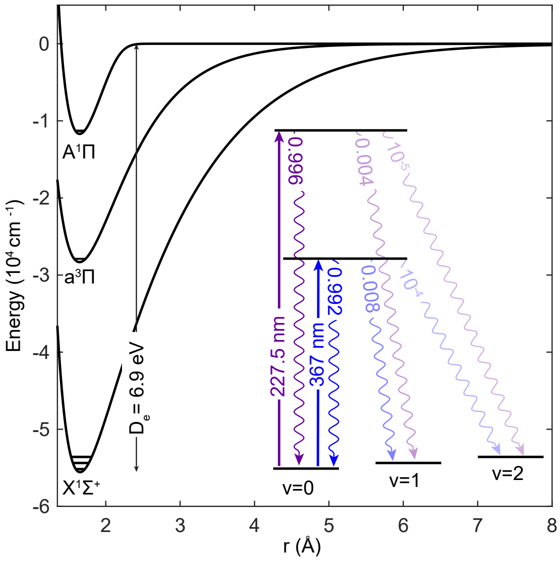

Figure 1: Calculated potential energy curves and Franck-Condon factors relevant for cooling and slowing of AlF.

In-silico Modeling of the HAMLET (Human Alpha-lactalbumin Made LEthal to Tumor cells) Alpha-1 Complex

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HAMLET (Human Alpha-lactalbumin Made LEthal to Tumor cells) is a tumoricidal complex of partially unfolded Alpha-lactalbumin and Oleic Acid [1]. The smallest subunit of Human Alpha-lactalbumin capable of forming tumoricidal complexes with oleic acid are it's alpha helical domains [2]. No high resolution structural model detailing atomistic interactions is available, despite experimental evidence characterizing the tumoricidal activity of the complexes. We used Hamiltonian Replica Exchange Molecular Dynamics simulations to sample the conformational landscape and model the interactions between the Alpha1 peptide derived from the Human Alpha-lactalbumin Alpha1 domain, and oleic acid. By comparison with a parallel simulation of the Alpha1 peptide alone, we show key differences in the free energy landscape of the Alpha1 peptide in the presence and absence of oleic acid. We show that oleic acid is required to stabilize the partially unfolded Alpha1 peptide in a dominant conformation. The dominant conformational model of the Alpha1 peptide-oleic acid complex is described as containing alpha-helical mortifs binding with the oleic acid in a hydrophobic core. This study provides atomistic insights into the interactions between the Alpha1 peptide and oleic acid, and proposes a structural basis for the tumoricidal activity of the complex.

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Periodic Trends of Spin-Orbit Heavy Atom on the Light Atom Effect to NMR Chemical Shifts Rationalized

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The importance of relativistic effects on the NMR parameters in heavy-atom (HA) compounds, particularly the SO-HALA (Spin-Orbit Heavy Atom on the Light Atom) effect on NMR chemical shifts, has been known for about 40 years. However, generally valid correlation between the electronic-structure of heavy element complexes and SO-HALA effect have been missing. By analyzing ^{1}H NMR chemical shifts of the 6th-period hydrides (Cs-At) we uncovered the basic electronic-structure principles and mechanisms that dictate the size and sign of the SO-HALA NMR chemical shifts.[1] In brief, partially occupied HA valence shells induce relativistic shielding at the light atom (LA) nuclei, while empty HA valence shells induce relativistic deshielding. The LA nucleus thus became relativistically shielded in $5d^2$-$5d^8$ and $6p^4$ HA hydrides and deshielded in $4f^0$, $5d^0$, $6s^0$, $6p^0$ HA hydrides. The introduced principles have a general validity across the periodic table and can be extended to non-hydride LAs as well. Moreover, the connection between the SO-HALA NMR chemical shifts and Spin-Orbit-induced Electron Deformation Density (SO-EDD) is derived. SO-EDD provides an intuitive understanding of the SO-HALA effect in terms of the depletion/concentration of the electron density at LA nuclei caused by spin-orbit coupling due to HA in the presence of magnetic field. Using an analogy between SO-EDD concept and arguments from classic NMR theory, the complex question of the SO-HALA NMR chemical shifts becomes easily understandable for a wide chemical audience.

Acknowledgement

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic under the National Sustainability Program I (LO1504). Computational resources were provided by the CESNET (LM2015042) and the CERIT Scientific Cloud (LM2015085).

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Ultracold rotational quenching of NCCN collision with ^{3}He and ^{4}He

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Abstract

Quantum mechanical scattering calculations[1] are performed for the rotational quenching of NCCN in collision with ^{3}He and ^{4}He using the close-coupling approach for collision energies between 10^{-6} and 200 cm^{-1}. Rotational quenching cross sections are computed in the ultracold region for rotational levels up to $j = 8$ using the He + NCCN potential energy surface[2] computed at CCSD(T)/aug-cc-pVQZ level of theory[3]. By averaging the cross sections over a Boltzmann distribution of velocities of the incoming ion, rate coefficients are obtained. Wigner threshold law[4] is found to be valid in ultracold regime where the cross-section exhibit inverse relation to kinetic energy. To further analyse the isotopic effect of He, we also computed the scattering lengths for rotational level of NCCN in the limit of zero temperature. The imaginary part of scattering length[5] is found to be very large for ^{3}He-NCCN. The results presented here will benefit future experimental studies of these or similar systems as methods to cool and trap neutral molecules.

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A GPU-accelerated implementation of DFTB+

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The requirement of accelerating calculations of complex chemical systems, i.e. molecular dynamics in the microsecond time scale, finds an answer in the use of GPUs. Here, a GPU-accelerated implementation of the software DFTB+ [1] is presented. The most-time consuming parts of the code are properly identified and ported to run on GPUs. Several benchmark calculations are carried out to assess the speed-up of the code, which show that the full potential and acceleration of the GPUs is only reached when the size of problem is large enough (matrices larger than 6000 × 6000).

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Mapping of exciton–exciton annihilation in a molecular dimer via fifth-order femtosecond two-dimensional spectroscopy

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We present a theoretical study on exciton–exciton annihilation (EEA) in a molecular dimer. This process is monitored using a fifth-order coherent two-dimensional (2D) spectroscopy as was recently proposed by Dostál et. al. [1]. Using an electronic three-level system for each monomer, we analyze the different paths which contribute to the two-dimensional spectrum. The spectrum is determined by two entangled relaxation processes, namely the EEA and the direct relaxation of higher lying excited states. It is shown that the change of the spectrum as a function of a pulse delay can be linked directly to the presence of the EEA process.

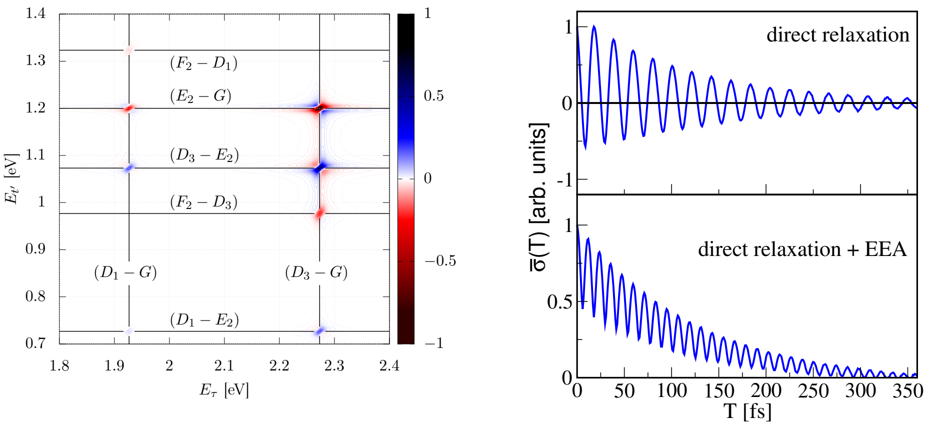

Figure 1: Left: Real part of the 2D spectrum including system-bath interactions. Right: Integrated signal $\overline{\sigma}(T)$ as a function of the population time T. The case of only direct relaxation is compared to the one where additional EEA is present.

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Incorporation of radionuclides in hydroxycarbonate and hydroxychloride green rust

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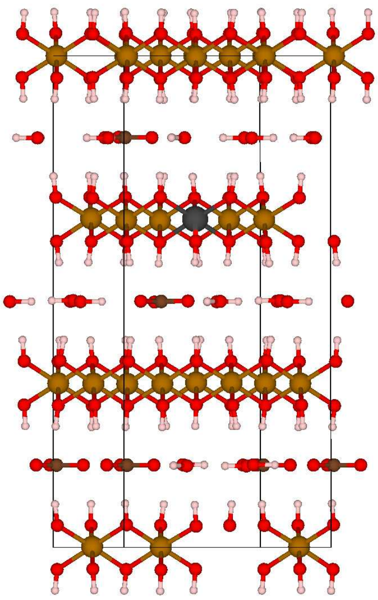

Figure 1: GR(CO_3^{-2}) .

Deep geological disposal is considered a prime solution for the safe management of high-level nuclear waste (HLW), such as spent nuclear fuel and waste from fuel reprocessing. In such deep facilities, the HLW will be confined in steel canisters which are foreseen to be surrounded successively by man-made (engineered) and natural (host rock) barriers.

Over extended period of time, ground water may reach the canisters which will corrode, resulting in the formation of secondary Fe phases and the establishment of reducing conditions. Typical corrosion products are mixed-valent Fe minerals [Fe^{II}/Fe^{III}] such as magnetite and green rust (GR). These mixed-valent iron minerals have received a significant amount of attention over recent decades, especially in the environmental sciences and play an important role regarding the mobility, toxicity, and redox transformation of organic and inorganic pollutants, such as radio nuclides.

In this study we focus on the incorporation of radio nuclides in hydroxycarbonate GR(CO_3^{-2}) [Fe_4^{II} Fe_2^{III} $(OH)_{12}]^{2+}$·[$(CO)_3^{(-2)}$·3H_2 O]$^{2-}$ and hydroxychloride GR(Cl^-) [Fe_3^{II} Fe^{III} $(OH)_8]^+$· [$(Cl)^-$·3$H_2O]^-$. We present density functional (DFT+U) calculations on both systems. From a theoretical side the presence of mixed-valence iron [Fe(II)-Fe(III)] ions in the brucite-like layers exhibits a major challenge. We find that the DFT+U method is very capable to determine the structural parameters as well as the magnetic properties of GR(CO_3^{-2}) and GR(Cl^-). In a second step we studied the incorporation of radionuclides, such as Ln^{3+}, An^{3+} and Iodide (I^-) into GR and compared with available experimental data [1,2].

Acknowledgement

KOSRO project, funded by the German Federal Ministry of Economic Affairs and Energy (BMWi) under contract no. 02 E 11496 B. VESPA II project, funded by the German Federal Ministry of Economic Affairs and Energy (BMWi) under contract no. 02 E 11607 C.

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Linear scaling reduction scheme based on pair-MP2 for periodic systems

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Contributions to the correlation energy at MP2 level are examined for a finite ring of hydrogen atoms. While it is true, that the most prominent terms are arising from doubly occupied pairs opposite in the reciprocal space, those pair terms alone are not sufficient to capture a fraction of MP2 that would be size extensive and not vanish at the thermodynamic limit. A physically motivated transformation of the mean field solution naturally separates the MP2 contributions into groups of very similar magnitudes. It is therefore possible to evaluate the mean value for each group and analytically integrate over groups of increasing size. The resulting approximation of MP2 is size extensive, has upper and lower bound on the error, and scales linearly from the number of basis functions. The method is thoroughly benchmarked against MP2 and CCSD with STO-6G and cc-pVDZ for closed shell hydrogen rings[1,2].

support from VEGA 1/0507/17 and UK/425/2019 kindly acknowledged

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Quantum and Semiclassical Instanton Theories for Chemical Reaction Rates

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We present a derivation of the quantum and semiclassical instanton expressions for the calculation of reaction rates. Starting from the exact expression for the reaction rate in terms of the flux-flux time correlation function, we use the steepest-descent approximation to obtain the quantum instanton expression, complete with the prescription for finding the optimal dividing surfaces. From the resulting quantum instanton expression, we semiclassically show that two paths contribute to the quantum instanton result, the standard semiclassical periodic orbit and a path which arises from the scattering solutions below the energies of the reactants. If we retain only the periodic orbit, we show that a semiclassical approximation to the quantum instanton results in the well-known semiclassical instanton expression. We show numerically that the quantum instanton prediction for the rate in a 1D asymmetric Eckart barrier potential breaks down severely for large asymmetries due to the contributions of the non-periodic paths. In contrast, the semiclassical instanton result remains accurate below the cross-over temperature. By neglecting the eigenfunctions below the reactant energies, we show that the quantum instanton method improves dramatically in accuracy. The result paves the way for a highly accurate version of the quantum instanton, which will then be a powerful method for calculating reaction rates in severely anharmonic multidimensional systems where the semiclassical instanton may not perform well.

Structure-property relationship of thermally activated delayed fluorescence (TADF) materials: Carbazole based organic emitters.

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Thermally activated delayed fluorescence (TADF) phenomenon has attracted a great deal of attention; triplet excitons can be harnessed via TADF in organic light emitting diodes (OLEDs), which leads to a low device fabrication cost. For an effective TADF phenomenon, the facile intersystem crossing (ISC) from the triplet to the singlet excited states is imperative; to this end, the singlet and triplet energy gap, ΔE_{ST}, should be considerably suppressed. It has been long believed that ΔE_{ST} is equivalent to $2K$, twice the exchange energy, and hence reduced via a spatial separation of the HOMO and LUMO. However, the singlet and triplet states are often of different nature, and the triplet states tend to favor the local excitation (LE) character, related to a large K value.[1]

In this presentation, based on the results of carbazole-based emitters, we will present how multiple carbazole units have influences on the nature of the triplet excited states, and thus the ΔE_{ST} values.[1] we will also discuss how such multiple molecular units can give rise to the quasi-degeneracy of the excited states and enhance the ISC rate.[2] Consequently, we propose a design rule for efficient TADF emitters.

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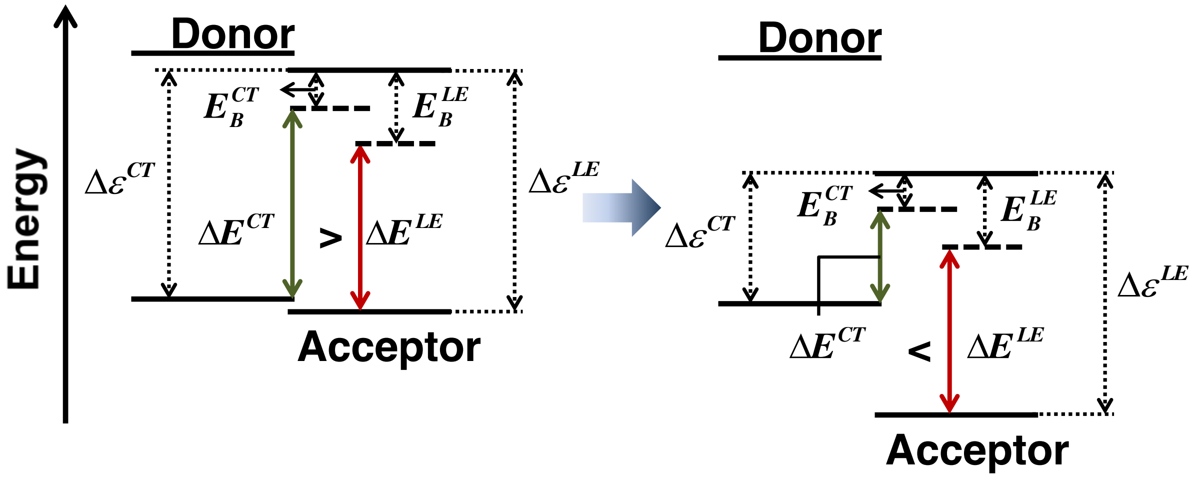

Figure 1: Schematic illustration of the evolution of the excited-state nature as a function of the HOMO and/or LUMO energy offsets between the donor and acceptor units.

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Revisiting the role of electrostatic interactions in the membrane binding of peripheral proteins

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Over the last decades, much effort has been dedicated into protein/protein or nucleic-acid/protein interaction mapping. However, the ways peripheral proteins interact with membrane lipids are poorly understood in spite of their crucial importance. The most widespread model of protein/membrane association described a two-steps mechanism: (1) the protein approaches the bilayer and orients under the influence of non-specific electrostatics forces and (2) the insertion of hydrophobic residues into the bilayer core. Former studies have established the importance of nonspecific electrostatic forces as a driving force for peripheral membrane association [1]. Nevertheless there is compelling evidence that some proteins display weak nonspecific electrostatics upon binding to lipid bilayers [2]. Using continuum electrostatics calculations, we identified 5 enzymes from the Orientation of Proteins in Membrane (OPM) database, which present unexpected electrostatics properties: a low electrostatic binding free energy and a negative electrostatic potential at their interfacial binding site. In order to understand which forces drive them to the membrane, we investigate the binding site of one of these enzymes: the phospholipase-D toxin from brown spiders. First, we ran multiple Molecular Dynamics (MD) simulations on phospholipase-D placing it away from different bilayer compositions. In all our MD simulations the protein managed to bind to the membrane, adopted the same binding orientation and stayed stably bound at the surface of the bilayer. The analysis of the MD simulations shows that aromatic amino acids especially tyrosines and tryptophans establish a high number of cation-π interactions with the lipid heads. These cation-π interactions are essential, as we observe no binding when we exclude these interaction terms from the molecular model we use. A low electrostatic interactions and the presence of various numbers of weak interactions, such as the cation-π interaction, can be useful for some enzymes, which need to unbind from the bilayer in order to find new substrates.

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Low-complexity MP2 for solids

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Hartree-Fock plus MP2 is a standard approach in materials physics and quantum chemistry to evaluate the energy of matter. However, this is computationally very demanding since conventional MP2 implementations scale with the fifth power of the system size, $O(N^5)$, and are difficult to parallelize. We present two low-complexity implementations that have a lower scaling and an almost ideal parallelization efficiency. The key concept of both approaches is to eliminate the summation over all combinations of occupied and unoccupied states, which can be elegantly achieved in the Laplace transformed MP2 formulation [1]. In this way we attain a quartic scaling high performance algorithm, $O(N^4)$, in the plane-wave basis without introducing further approximations. Moreover, using stochastic HF orbitals, a cubic scaling, $O(N^3)$, can be achieved when a fixed absolute error is assumed which turns into a linear scaling, $O(N)$, when only a fixed relative error is assumed (e.g. per atom) [2, 3]. Analogously, the approaches could allow us to calculate second-order screened exchange as well as particle-hole ladder diagrams with a similar low complexity.

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Calculation of redox potentials for iron-sulfur proteins

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Metalloproteins are key components to energy transduction in several biochemical pathways through redox reactions. Here, we investigate isolated models of iron-sulfur cofactors and a simple protein, rubredoxin, in an all-atom framework to identify the main physical contributions to the calculation of redox potentials employing QM/MM hybrid methods. Calculations in an ionic force (salt, NaCl) setup presented poor convergence due the challenging sampling of ion configurations. A proper description of the polarization around the redox center is required and demands a large quantum region of up to 200 atoms around the central iron-sulfur center. Finite model effects, level of quantum-mechanical treatment, explicit hydration of cofactors and configurational sampling were also evaluated.

Poster: P2-5

Electronic Coherence in Ultrafast X-Ray Scattering by Molecules

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Recent advances in the preparation of intense, ultrafast, and coherent pulses of hard x-rays permit the observation of dynamics in atoms and molecules in real time *via* non-resonant scattering. The elastic component of the scattering signal is well known to provide information about time-dependent changes in the molecular one-electron density as a result of nuclear motion. The inelastic component, in contrast, is usually not considered, as it is commonly assumed that inelastic scattering does not depend on the nuclear geometry and thus time. Contesting the generality of this assumption, we have shown that the inelastic component can be time-dependent as well.[1] Extensive simulations of ultrafast x-ray scattering by a nuclear wave packet in the hydrogen molecule have demonstrated that the inelastic component changed significantly in the course of the nuclear dynamics. Moreover, pulses generated at new X-Ray Free-Electron Laser facilities may enable the detection of a third component in the scattering signal that we have termed *coherent mixed*. It is caused by an intramolecular interference of scattering amplitudes of at least two electronic states that are coherently populated. In their groundbreaking paper, Dixit *et al.* have shown that the ultrafast x-ray scattering signal of an electronic wave packet in the hydrogen atom is not just given by the Fourier transform of its one-electron density.[2] In essence, it is the coherent mixed component that led to the time-dependent signal Dixit and his coworkers have reported.[3] The coherent mixed component was furthermore addressed in seminal work by Mukamel *et al.*, who have demonstrated that the component can carry a distinct signature of non-adiabatic population transfer in the vicinity of an avoided crossing.[4,5] We have recently published the first two-dimensional coherent mixed scattering patterns of a molecule and showed that they provide a direct probe of the degree of electronic coherence.[1] It is thus likely that information beyond pure structural dynamics can be obtained from ultrafast x-ray scattering experiments in future.

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Study of photo-ionization processes using Full Configuration Interaction Quantum Monte Carlo

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The real time Full Configuration Interaction Quantum Monte Carlo (FCIQMC) method has recently been developed to solve the time-dependent Schrödinger equation stochastically and applied to calculate electronic spectra for many-electrons systems [1]. The application of real time FCIQMC is extended here to treat the photo-ionization processes of atoms. The use of full Hilbert space in FCIQMC allows to capture the interplay between two or more electrons in an atom which is important in describing the photo-ionizations processes accurately. One of the main challenges in treating the photo-ionization process is to get accurate descriptions of both the bound and the continuum states for an extensive space of region. We, therefore, have used numerical grid-points as basis obtaining them following the Finite Element Discrete Variable Representation (FE-DVR). In this work, we present the application of FCIQMC in obtaining ground state energies for atoms using the FE-DVR basis and on studying photo-ionization processes thereafter.

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Spin Projection made easy

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The use of projected wavefunctions has gained attention in recent years, from the original work of Scuseria et al. [1], by providing a Projected Hartree-Fock theory, several extensions of the method have appeared. Especially promising is the application to post-PHF methods, like to single and double excitations in the CI method [2]. In all these applications the projected wavefunction is attained by expressing the projector operator in integral form and performing a numerical integration over a gauge angle.

In the present work [3] we propose to use the Löwdin projector, this is a clear (and robust) way to recover the spin symmetry of a UHF determinant, $\widehat{\mathcal{P}}_S |\Psi_{\text{UHF}}\rangle = \sum_k C_k(S)\,|T_k\rangle$. However, its naive application is not computationally feasible, since it requires considering all spin-flipped determinants. To overcome this difficulty, we show that introducing a formal parameter, that collection can be recast into a single determinant. The fundamental result states that the sum T_k of all determinants with k spin-flips corresponds to the coefficients of the following polynomial

$$\sum_k \langle \Psi_{\text{UHF}} | T_k \rangle \, z^{\nu-k} = \begin{vmatrix} \mathbb{I}_\mu & \mathbf{S} \\ \mathbf{S}^\dagger & z \cdot \mathbb{I}_\nu \end{vmatrix} , \tag{1}$$

where $S_{ij} = \langle \phi_i | \theta_j \rangle$, i.e. the overlaps between *up* and *down* spatial orbitals. This result is used to derive compact expressions for operator matrix elements over spin projected wavefunctions, resulting in a *Projection After Variation* scheme where the projection is carried out exactly, removing all spin contaminants. It is suitable in cases when the reference determinant has contaminants of many different spins. This procedure could be considered as an alternative to the more general method of *Analytic Energy Gradients* applied to the projection of $\hat{S}^2$ [4]. Having expressed the combination of determinants as a single entity permits to optimize the orbitals by requiring them to minimize the projected energy, leading to a Pople-Nesbet alike system of equations. The application of the formalism to the CI method has been also considered.

We apply our results to circularly confined quantum dots, and (possibly) under the influence of a magnetic field. In such systems, spin symmetry, as well as rotational symmetry restoration methods have proved to be a valuable technique [5]. To allow for a simultaneous restoration of the circular symmetry the method has been extended. We show how the (spatial-) RHF method fails to predict the L_z and S_z quantum numbers of the ground states for a large region of the magnetic field strength and Wigner parameter (measure of the relative strength between electron-electron interaction and confinement). While the quantum numbers from projecting broken symmetry determinants agree quite well with the prediction of Full CI calculations.

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Systematic Evaluation of Reaction Field Schemes for Coupling COSMO Polarizable Continuum Model and Second-order Wavefunction Methods for Computing Solvatochromic Shift

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A reaction field is an electrostatic field G[D] generated from the interaction of the solute charge distribution D and a polarizable environment. For post-HF methods, various schemes have been introduced to describe the interaction between the correlated part of the wavefunction of the QM system and the polarizable environment. In this study, the assessment of three reaction field schemes, including the perturbation on the energy-only scheme (PTE), the iterative perturbation on the energy and density scheme (PTED) and the post-SCF scheme, Fig. 1, were considered for the calculation of solvatochromic shifts. We composed two benchmark data sets and compared the solvatochromic shifts resulted from the experiment and theory.

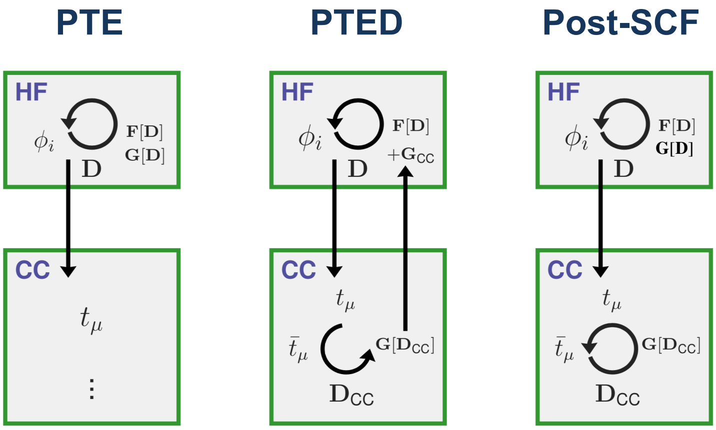

Figure 1: Reaction field schemes in coupled cluster theory.

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Topological Data Analysis in quantum chemistry - the electron density of Au complexes case study.

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We demonstrate the use of the Topological Data Analysis (TDA) for the electron density (ED) of Au complexes evaluated at different levels of accuracy. TDA tracks the evolution of critical points of data, hence if applied to ED, it has a direct connection to the Quantum Theory of Atoms in Molecules (QTAIM). Our study contributes to the discussion of the use of QTAIM for the non-covalent interactions, especially in relativistic regime, and proposes to consider TDA as a modern complement to QTAIM.

Excited-state machine learning molecular dynamics simulations on nanosecond time scales

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Many important processes in nature and life on earth are photo-induced. To unravel fundamental mechanisms at the basis of these processes, excited-state ab-initio molecular dynamics simulations can be carried out, that describe the motion of a molecule after its excitation with light. As undoubted as the importance of this method is its limitation to short time scales, which is due to the unfortunate cost of the underlying on-the-fly quantum chemical calculations [1]. In this work, we circumvent this bottleneck by machine learning algorithms, that speed up simulations up to a factor of 4000 and make nanosecond molecular dynamics simulations possible within only a couple of days [2]. As an example, we show the surface hopping molecular dynamics simulations of the methylenimmonium cation. We also treat spin-orbit and nonadiabatic couplings of additional molecules with up to 66 degrees of freedem, for which we generated reference data by random grid sampling and an adaptive sampling scheme [2,3]. In order to render the reference data learnable, we apply a phase correction algorithm that tracks the phase of the electronic wavefunctions from one reference point to every other configuration inside of the training set. For dynamics simulations and the computation of wavefunction overlaps we utilized the program suite SHARC (Surface Hopping including ARbitrary Couplings)[1,4]. To further guarantee that our machine learning models predict the potential energy surfaces and corresponding properties correctly, we apply an active learning approach similar to reference [5] by using two models and comparing their outputs on-the-fly. As machine learning models we use multi-layer feed forward neural networks [2] and the deep learning model SchNet [6] that show the scopes and possibilities for treating different excited-state characteristics with high efficiency and on long time scales.

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A Semiclassical Glimpse into the Azulene Photophysics and Spectroscopy

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Azulene molecule is a prototype system violating Kasha's rule, *i.e.,* its fluorescence occurs from the second, instead of the first excited singlet state [1]. To study the role of nonadiabatic couplings that cause the unusual fluorescence behavior in azulene, we compute the semiclassical fidelity (*i.e.* adiabaticity) *via* multiple surface dephasing representation method [2] combined with on-the-fly *ab initio* evaluation of the potential. Adiabaticity measures explain the different dynamical behavior of the lowest excited states in azulene. The analysis was compared to the standard measures from nonadiabatic dynamics, such as state population decay. Azulene absorption and emission vibronic spectra cannot be properly described within the standard Condon approximation [3]. To account for important Herzberg-Teller and anharmonicity effects, we employ a single-Hessian [4] version of the on-the-fly *ab initio* extended thawed Gaussian approximation [5], which compares fairly well with the experimental reference.

Overall, two semiclassical approaches provide efficient tools to tackle the photophysics and spectroscopy of challenging molecular systems.

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Theoretical approach for simulating single photon double core ionization of small molecules

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Double core hole states (DCH states) have been observed as the result of single photon absorption at synchrotron facilities. Still the experimental observation of the formation of these highly excited system remain a challenge mostly because of the very low probabilities of such events (few order of magnitude lower than standard single core hole formation). In this context, developing robust theoretical approach for simulating these events is crucial in order to filter what is actually a signal from what is merely an experimental noise and to assign a final DCH state (the main close shell one and all its valence-valence shake-up excitation satellites) to the coresponding peak.

In the dipolar approximation, the corresponding cross section is proportional to the square of the overlap matrix between the neutral initial state and the K^{-2} double core ionized final state. We show that using the CIPSI [2] selected CI method for computing both initial N electrons and final $N-2$ electrons wave functions lead to good accord between our simulated spectrum and experimental results for small molecules such as (O K^{-2}) CO (Fig.1) and H_2O. We also show that using the second order Epstein-Nesbet perturbative correction to the energy naturaly available in the CIPSI methode leads to a fast convergence of the peak relative energies. For instance in the case of the CO molecule it reduces the number of selected slater determinants needed in the expansion of the ion wave function to achieve convergence from 3.5 million to a mere 500 000 determinants significantly reducing the numerical cost of such calculation.

Finally we show that using two non-orthogonal molecular orbital (MO) basis set for the neutral and the ion wave functions, and using Löwdin rules [3] to compute the overlap, lead to a faster convergence of the peak intensities compared to the case where we use the same MO basis for both, further reducing the numerical needs.

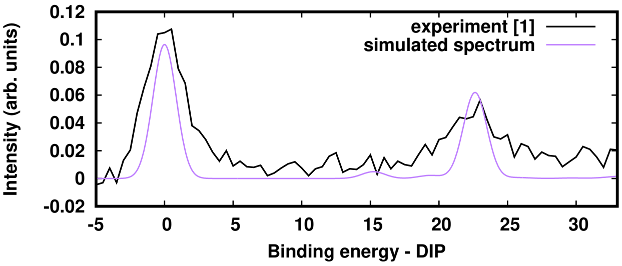

Figure 1: Computed and experimental O(K^{-2}) spectrum of the CO molecule.

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Two- and three-body energies from the DLPNO-CCSD(T) method

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Domain-based local pair natural orbital coupled cluster theory with single, double, and perturbative triple excitations [DLPNO-CCSD(T)] method [1] was applied to calculations of two- and three-body intermolecular interactions energies of several van der Waals complexes. The results were compared with the coupled cluster method with single, double and non-iterative triples excitations with the complete basis set extrapolation [CCSD(T)/CBS] benchmarks and several density functional theory plus dispersion approaches (DFT-D) [2,3]. The accuracy of the DLPNO-CCSD(T) method for two-body interaction energies was tested with several local cutoff thresholds with both orbital basis sets and with explicitly correlated DLPNO-MP2-F12 method [4] used with a DLPNO-CCSD(T) correction. The large computational speed-up of the DLPNO-CCSD(T) method compared to the canonical CCSD(T) method is followed by decrease of the accuracy but the the quality of the two-body energies was found to be competitive with the DFT-D methods. For three-body non-additive energies, the DLPNO-CCSD(T) offers similar overall accuracy to the MP2 method, a rather disappointing result considering the lack of non-additive dispersion in the supermolecular MP2 approach. On the other hand, for three-body energies, the DFT-D methods do not work, either [5]. Overall, DLPNO-CCSD(T) can be to some extend used for intermolecular interactions after careful selection of cutoffs and basis sets.

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The *effective* modeling of photobiology with the Effective Fragment Potential method

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Accurate description of solute-solvent interactions is an essence for modeling and understanding of photochemical processes in biological systems. The Effective Fragment Potential (EFP) is a quantum mechanical-based model potential providing rigorous description of non-covalent interactions from first principles. In biological systems where intermolecular interactions span a broad range from non-polar to polar and ionic forces, EFP is superior to classical force fields. With the presence of *ab initio* region, EFP-based QM/MM schemes (so called QM/EFP) describe biological environment with explicit inclusion of polarization. In the present study, we elucidate excitonic interactions in the Fenna-Matthews-Olson (FMO) photosynthetic pigment-protein complex with the QM/EFP approach. In photosynthetic genus, the FMO complex transfers the excitation energy from light harvesting antenna chlorosome to the reaction center with high efficiency. We demonstrate that QM/EFP absorption and circular dichroism spectra of the FMO complex are in good agreement with experiment. Building upon these results, we characterize effects of local amino acids and of long-range electrostatic and polarization interactions on the electronic properties of *bacteriochlorophyll a* (*Bchl a*) pigments. We also find that internal geometries of pigments are strongly coupled with several neighboring amino acids and accurate description of pigment geometries is essential for predicting excitonic interactions in the FMO complex.

Classification of Rotational Energy Levels within the Complete Nuclear Permutation Inversion Group

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For the classification of molecular energy levels and spectroscopic transitions group theory is an important tool. Whereas for rigid systems conventional point group concepts are usually sufficient, for non-rigid systems, in which for example tunneling has to be considered, the more general concept of permutation-inversion groups is needed.[1] The complete nuclear permutation and inversion (CNPI) group, which includes all permutations of identical nuclei, however has the disadvantage, that it is very large even for small molecules. Therefore subgroups, which only include feasible permutations, are usually used.

We use a system of 4 atoms as a minimal example for symmetry classification of rotational energy levels of a chiral system within the CNPI group. Within this group restrictions due to nuclear spin can be included as well as splitting of energy levels due to tunneling between enantiomers or between different versions of the enantiomer.

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Static polarizabilities at the basis set limit: A benchmark of 128 species

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Multiwavelets have been shown to deliver atomization energies [1] and magnetic properties [2] at the complete basis set limit (CBS). In this work we extend the use of multiwavelets to the calculation of static polarizabilities (StatPol) for a set of 128 small molecular and atomic species. By comparing to highly accurate multiwavelet results, we have quantified the basis set errors present in StatPol calculations with the large GTO basis set aug-pc-4 [3]. With the MRChem program package, we used the finite difference approach to obtain StatPols, and all comparisons were done with the PBE functional. We find that the large GTO basis generally performs well, resulting in relative deviations of less than 0.5 % for the majority of the species (Figure 1). However, several challenging cases are revealed, especially among the open-shell species, where relative deviations as large as 8 % are observed. Note that a portion of these larger deviations are likely due to contamination from hyperpolarizabilities, due to the large field strength of $\epsilon = 0.01$ used in the GTO calculations. Further, GTOs seem to overestimate the StatPols, which goes against intuition as analytical StatPols are variationally approached from below. In sum, it cannot be assumed that large GTO basis sets are sufficiently close to the CBS when computing StatPols for open-shell species, and multiwavelets provide the possibility of obtaining quasi-exact results with respect to the CBS. The contributions from hyperpolarizabilities also need to be quantified in order to provide a fair comparison of GTOs and multiwavelets.

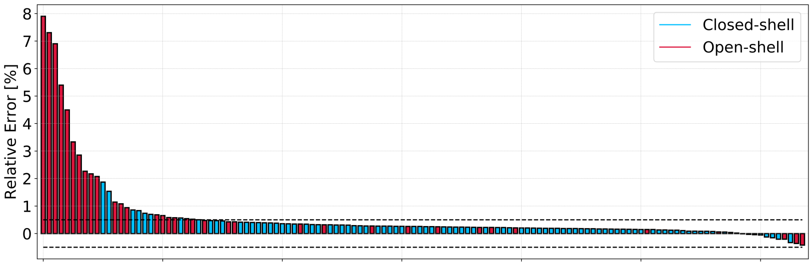

Figure 1: Distribution of relative deviations for all 128 species. The dashed lines are located at ±0.5 % relative deviations.

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Periodic orbits localization through energy frequency analysis in bound systems

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Density of states (DOS) plays a central role in statistical physics. The knowledge of DOS is essential to characterize semiconductors, bio-systems, rate processes and to calculate partition functions. The calculation of the exact DOS is complicated because in the general case the energy levels of molecular systems are unknown. In practice we need to separate the different degrees of freedom and treat the system in the rigid rotor and harmonic picture to evaluate the DOS. In absence of anharmonicities and ro-vibrational couplings this static treatment of the problem results a poor description of the DOS. A dynamical treatment of the problem would be needed to include all of this missing factors. Molecular dynamics is an elegant way to calculate the vibrational spectrum of molecules to include the all of the anharmonicities, the couplings between vibrational and rotational modes and the contribution from large amplitude (torsional) motions.

In our work we have developed a molecular dynamics based approach where the kinetic energy spectrum is used to localize the periodic orbits. An extended normal mode like ansatz is introduced to decompose the phase space into harmonic periodic orbits. The kinetic energy spectrum is fitted by this ansatz to extract the fundamental frequencies of the system. Such kind of representation of the dynamics allows to preserve the simple normal mode like picture by renormalizing the harmonic frequencies. However, now the frequencies depend on the total energy and angular momentum of the system: $\omega(E, J)$. The evaluation of the DOS is straightforward by using the renormalized harmonic frequencies. Furthermore, our approach is a natural way to characterize the coupling between the renormalized harmonic modes.

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The effect of molecular geometry on He*-H_2 autoionization reaction

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A new technology developed by Ed Narevicius [1,2] enables chemical reactions to proceed at very low temperatures, close to absolute zero. For example, a Penning ionization reaction was observed on the collision of an excited helium atom and a hydrogen molecule. The investigation of such reactions is enabled by generating a complex potential energy surface (CPES). In our research, using CPESs obtained by Bhattacharya and coworkers [3], we study the Penning ionization reaction rate during the collision of He^* (^3P,1s2p) and H_2 as related to their geometry. Our results demonstrate that due to the large anisotropy of the CPESs, the molecular geometry during the ionization reaction observed in the experiment, was almost exclusively the B_1 T-shape geometry, although the ionization could theoretically occur also in the other geometries. Figure 1 shows an excellent agreement between the reaction rate coefficient calculated assuming the B_1 symmetry of the T-shape geometry (without any fitting or scaling parameter) and the measured coefficient. The reaction rate coefficients for each geometry were calculated using a simple closed-form expression [4], which yielded a good agreement with the experimental results of the collision between He^* (^3S,1s2s) and H_2 [5].

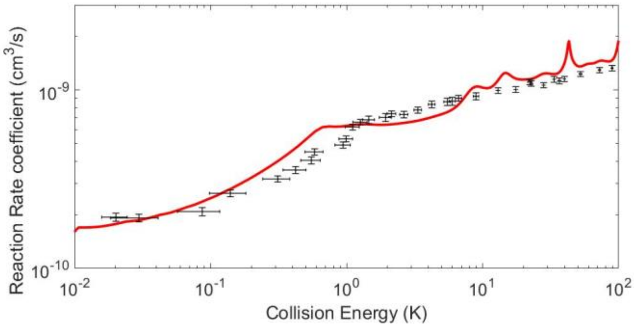

Figure 1: Comparison of the measured reaction rate coefficient with the coefficient calculated assuming the B_1 T-shape geometry (in red).

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Frozen-pair Coupled Cluster methods for strong and weak correlation

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The major part of the strong correlation can be provided by the pair Coupled Cluster Doubles (pCCD) model combined with a (variational) orbital optimization protocol [1,2]. The orbital-optimized pCCD method is size-consistent and computationally inexpensive in comparison to various multi-reference approaches. However, it does not account for all electron correlation effects. [3] One way to include the missing (dynamic) electron correlation effects is to use a (linearized) Coupled Cluster correction on top of the pCCD wave function. [4,5] The frozen-pair Coupled Cluster Singles Doubles (fpCCSD) method is one efficient way to improve the wave function with the cost of CCSD. [4] In fpCCSD or its linearized variant, the singles and non-pair doubles amplitudes are optimized, while the pair doubles amplitudes are kept frozen. Such an optimization routine provides a balanced description of strongly-correlated systems, where traditional CCSD usually fails. In this work, we will scrutinize the performance of various Coupled Cluster corrections on top of pCCD.

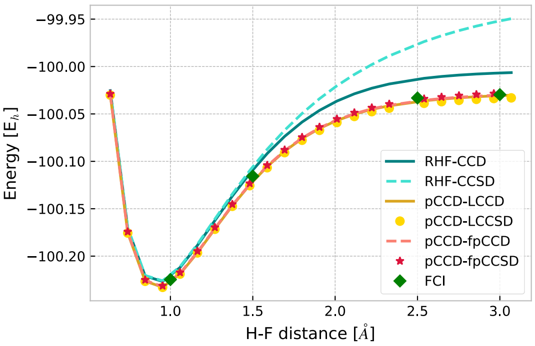

Figure 1: Potential energy curves of fluorine molecule (cc-pVDZ basis set).

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Separation of Density-Driven and Functional Error of Density Functional Calculations via Kohn-Sham Inversion

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Despite the success of Kohn-Sham density functional theory (DFT)[1], the approximate nature of exchange-correlation energies and potential functionals in DFT provides only approximations to physical and chemical properties. Therefore, the role of approximate exchange-correlation potentials that generate the corresponding electron density is critical. However, the approximate exchange-correlation potential behaves untraceable during self-consistent procedures. As a result, some *abnormal* calculations can result in errors in the self-consistent electron density, causing severe energy errors. One example is the dissociation of hetero-diatomic molecules.[2] To improve functional approximation and ultimately achieve the universal functional, individual analysis of energy errors from the density error and the functional approximation is important. However, it is usually not easy to quantitatively separate the energy errors due to inaccurate electron density (density-driven error) and incorrect energy functional (function error). Here we quantify density-driven and functional errors using fairly accurate electron densities from high-level *ab-initio* calculations. The technical problem of this procedure is the calculation of Kohn-Sham kinetic energy, and we employ the Kohn-Sham inversion technique using the methods proposed by Zhao, Morrison, and Parr[3] and by Wu and Yang[4]. For local functionals such as LDA and GGA, we found that there is a delocalization error in both density and functional (i.e., energy), but the error ratio varies depending on the system. For global hybrids, although a particular system-specific portion of the exact-exchange appears to make the total error zero, which arises through cancellation between the density-driven and functional errors rather by zero density-driven error and zero functional error. We show that such error cancellation is not uncommon and demonstrate the importance of systematic analysis using error decomposition.

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DFT Studies on Mechanism and Reactivity of Radicals generated from Boronic Esters

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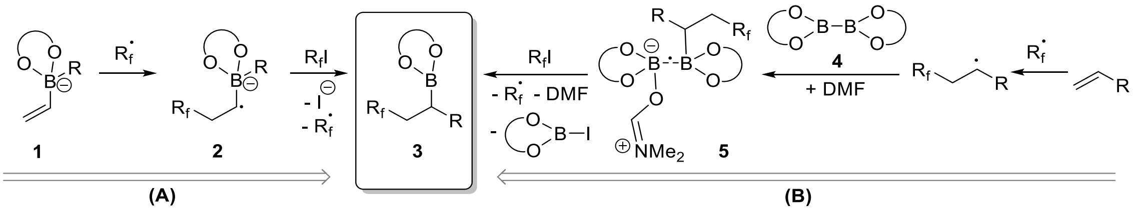
Recently, new synthetically useful radical reactions involving the boronic ester group -B(OR)$_2$ have been developed. The addition of two alkyl groups (R, R$_f$) to a vinyl group can be achieved starting from vinyl boronic esters in a radical-polar crossover process (**A**).[1] Similar products (**3**) are obtained in the reaction of bis(catecholato)borane **4** with a radical formed by the addition of $^{\cdot}$R$_f$ to substituted alkenes (**B**)[2]. Both mechanisms regenerate the initial radicals and the reactions are thus conducted as chain processes. In the absence of an alkene, the reaction of bis(catecholato)borane with a radical allows the metal-free borylation of alkyl and aryl iodides.[3]



We have conducted DFT studies on the mechanism of these reactions and discuss the reactivity and characteristic properties of radical intermediates such as **2** and **5**. The latter adduct (**5**) is remarkable as it contains a boron-boron one-electron σ bond and is stabilized by a solvent molecule (Figure 1).[2]

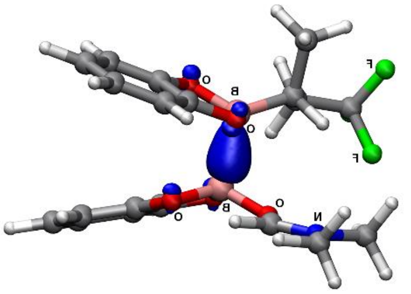


Figure 1: Spin Density Distribution (0.02 a.u.) of Radical **5** (PBE0/def2-TZVP)

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Tetraoxa[8]circulene-Based Nanosheets as a New Family of Two-Dimensional Covalent Metal-Free Organic Frameworks

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The structural and electronic properties of a new family of two-dimensional (2D) covalent metal-free organic frameworks based on tetraoxa[8]circulene (TOC) with different types of fusing have been studied. All nanosheets demonstrate high thermodynamic stability and unique electronic properties depending on the fusing type. Among three types of nanosheets, only two of them demonstrate semiconducting properties exhibiting 1.37 and 1.84 eV direct band gaps, while another one was found to be a semimetal, which possess strong topological states. We have found that spin-orbit coupling effects enhance the band gap (~87 meV) for the studied material and this effect exceeds by several orders of magnitude relative to the graphene analogue. Tetraoxa[8]circulene-based nanosheets are also predicted to be good organic semiconductors due to a clearly observable quantum-confinement effect on the band gap size in oligomers and relatively low effective masses, which result in high carrier mobility. Owing to the versatility of chemical design, these materials have the potential to expand applications beyond those of graphene.

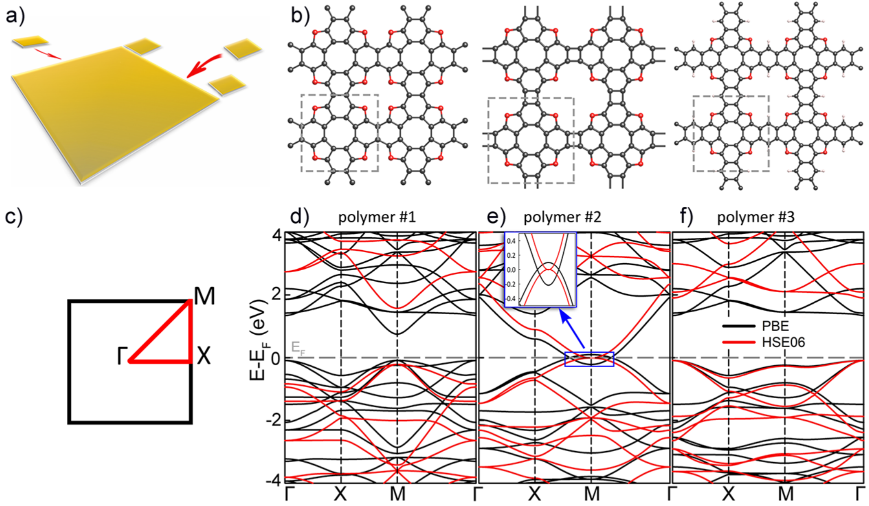

Figure 1: Illustration of 2D TOC formation (a) via attaching the same monomers in different ways (from left to right: polymer#1, polymer#2, and polymer#3 (b). Unit cells are marked by dashed gray lines. Carbon, oxygen, and hydrogen atoms are presented in black, red, and beige, respectively. The high-symmetry k-points (c) in the Brillouin zone and corresponding electronic band structures calculated by GGA-PBE (black lines) and HSE06 hybrid functional (red lines) for polymers#1 (d);#2 (e); and#3 (f). The inset shows the frontier states behavior near the Fermi level in polymer#2.

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Theoretical Insights to Coordination Chemistry of Carbon: Novel Bonding and New Organic Chemistry

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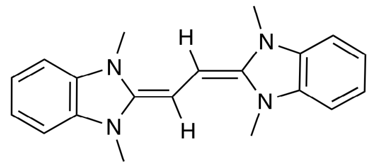
Consideration of coordination chemistry of carbon, whereby carbon acts as a Lewis acidic centre stabilized by donor ligands, has led to an emerging new field of organic chemistry. Here we report outcomes from theoretical and experimental studies, employing N-heterocyclic carbene (NHC) and cyclic alkyl-amino carbene (CAAC) ligands, to stabilize various C_2 containing fragments [1]. We have discovered a form of ligand-stabilized acetylene (1) [2], featuring a formal double bond that is weaker than a typical C-C single bond [1], and the first example of a diorganoalkene that prefers to adopt a cis- configuration (2) [3-4]. The electronic structure of these systems has been investigated with MO, NBO, QTAIM, I-SAPT, and EDA analyses, to provide an understanding of electronic structure, bonding, and non-covalent interactions. The focus of this presentation will be on the electronic structure and bonding description of these novel species.



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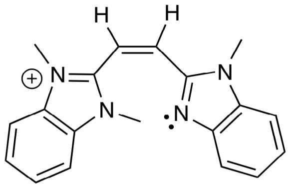

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Advancing CAP-EOM-CCSD scheme for electronic resonances: projected CAP scheme and Voronoi absorbing potential.

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Chemical conversions initiated by electron-molecule interactions or photo-excitation can involve formation of auto-ionizing *resonances* as gateway states. Theoretical description of these metastable electronic states requires reliable information on energetics and lifetimes, which cannot be obtained using conventional bound-state electronic structure techniques. The *complex absorbing potential* (CAP) is a powerful non-hermitian technique which can be paired with bound-state electronic structure methods to calculate resonance positions and widths for molecular systems[1]. Two important practical considerations for this methods are the form of the absorbing potential and the level of theory in which the CAP is engaged, as both choices can significantly affect the results. Here, we present a study of the effects the CAP shape and its level of treatment have on the results of EOM-CCSD calculations of resonance position and width. Specifically, we have implemented the Voronoi CAP, which depends explicitly on nuclear coordinates and wraps around the system similar to a van der Waals surface[2], for CAP-EOM-CCSD scheme and compared its performance with the standard box CAP. The scheme was tested on three types of systems: diatomic molecules, a localized resonance in a cluster, and a delocalized resonance. We also have compared two ways of treating the CAP: explicit, when CAP is included starting from HF stage of calculation, and perturbative when CAP is treated in first order of perturbation on the results of EOM-CCSD calculation (projected CAP). The second scheme allows one to obtain the estimates of resonance position and width at a cost of single electronic structure calculation. The results of benchmark calculations on a set of representative shape resonances in molecular systems are presented.

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On-the-fly *ab initio* semiclassical evaluation of electronic coherences in polyatomic molecules

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Ionization of molecules very often leads to simultaneous population of several cationic states launching thus pure electron dynamics that appear as ultrafast migration of the hole charge throughout the system. A crucial question in the emerging field of attochemistry is whether these pure electronic coherences last long enough to allow for their efficient observation and eventual manipulation with ultrashort laser pulses.

In order to address this question a full quantum treatment of the coupled electron-nuclear dynamics is required. Despite the fact that such calculations were recently performed using MCTDH-based approaches for several small molecules [1-3], it is still very case specific and requires construction of global PES, which is a daunting task by itself.

In contrast, approximate semiclassical methods can be used in combination with on-the-fly evaluation of the electronic structure which allows to avoid the exponential scaling problem. One of the simplest, yet efficient, semiclassical approaches for molecular dynamics is provided by the thawed Gaussian approximation (TGA) developed by Heller and co-workers [4]. Within this approach, the nuclear wavefunction is described by a single Gaussian wave packet whose time-dependent width is propagated using the local harmonic approximation of the PES.

Here we present a semiclassical TGA calculations of the electronic coherences initiated by outer-valence ionization of propiolic acid molecule. A very good agreement between fully quantum MCTDH calculations and semiclassical TGA results is demonstrated. We argue that simple semiclassical schemes can be efficiently used to support theoretically recent experimental studies of ultrafast electronic dynamics in realistic molecular systems.

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Poster: P2-26

Optical signals of photosynthetic antenna complexes modulated by microsecond protein dynamics

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The plant antenna complex light-harvesting complex II (LHCII) is a key player in natural photosynthesis. LHCII occurs as a trimeric protein complex and contains 42 chlorophylls. Its chromophores are responsible for capturing photons and transmitting the excitation energy towards the photosystem II reaction center. This challenging task requires a highly precise chromophore arrangement resulting in a specifically fine-tuned ordering of the energy levels and couplings.

We built a coarse-grained (CG) model of LHCII using the Martini force field which allows us to study the LHCII dynamics in the thylakoid membrane on a hundreds of microseconds time scale (Fig. 1a) [1]. Using tools from machine learning, we extracted the most prominent structures (Fig. 1b) via a density-based clustering algorithm. The chlorophyll arrangements of these structures are used to calculate the electronic couplings between the chlorophylls by means of the extended dipole model. Based thereon, we use an excitonic Hamiltonian to simulate linear absorption, circular dichroism (Fig. 1c), and two-dimensional electronic spectra.

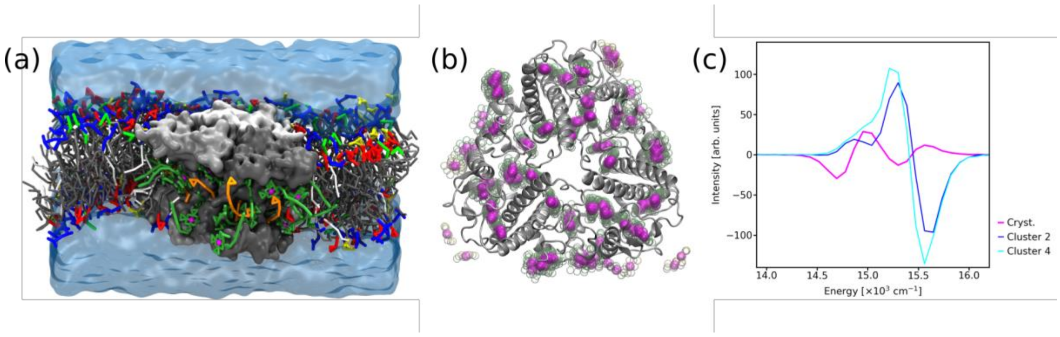

Figure 1: Simulation box containing a LHCII trimer in thylakoid membrane (a), extracted clusters from a 10 µs CG MD trajectory (b), circular dichroism spectra for the two most prominent clusters and the crystal structure (c).

Our study shows that the sampled configurations of trimeric LHCII span a manifold of chromophore arrangements. Moreover, these individual arrangements have a pronounced impact on the optical properties of LHCII trimers. We will discuss the impact of the microsecond protein dynamics on the electronic spectra of LHCII and to which extent the protein matrix dynamics results in an increased diversity of excitonic conditions for the excitation energy transfer.

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Decrypting Photoinduced Electron Transfer in Cryptochromes: First-Principles Study

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Predictive and quantitative simulation of the photoinduced electron transfer (PET) in biological systems remains a challenge for modern computational chemistry. Proper characterization of ET requires (i) identifying the active players and establishing the efficient channels in the cascade of ET processes, and (ii) quantifying thermodynamics and dynamics of ET events. Here, we present the results of multi-level computational study of PET in cryptochromes, involved in circadian rhythms, growth and development processes in plants, and magnetosensoric mechanism in migratory birds and insects [1]. We exploit multiple computational chemistry methods targeting various aspects of ET process at different levels from empirical coarse-grained description to atomistic QM/MM simulations. Specifically, we first use our recently developed web application [2] to identify all existing chains of aromatic amino acid side chains, cofactors and metabolites that can serve for efficient electron/hole hopping [3]. We then employ the accurate first-principles electronic structure methods to compute model parameters of sites of interest for an ensemble of local minima sampled with the classical MD and locally optimized at QM level in the presence of MM environment. The energetic parameters are extracted from QM/MM simulations using density functional theory, post-Hartree-Fock methods, and a recently developed extension of effective fragment potential approach to macromolecules (mEFP/BioEFP) [4, 5], which takes into account the effects of environment polarization, crucial in redox [5, 6] and charge transfer/separation processes. The computed from the first-principles parameters are utilized for evaluating efficiency of the first ultrafast step of competing conventional and alternative ET pathways [7, 8] by calculating the time scales and quantum yield from the population dynamics, using semiclassical path integral methods in combination with the accurate approach to describe relevant electronic-nuclear interactions [9]. The obtained results indicate that photoexcitation can initiate several competing ET channels, and contribute to understanding of complex PET processes accompanying formation of photoactivated state of the protein *in vivo* and *in vitro* in diverse systems including cryptochromes in plants, birds, and humans.

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Poster: P2-28

Acenes and their fluorinated derivatives as model systems for singlet heterofission

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To overcome the so called Shockley-Queisser limit in photo voltaic cells, the process of singlet fission[1,2] is of high interest in experimental and theoretical studies. By generation of two triplet excitons from one singlet exciton, one can achieve better conversion efficiencies. Therefore the aim is to understand the process of bi-exciton generation and to design new model systems with better singlet fission rates.
The process can be described by the following simplified scheme:

$$\mathrm{S}_1 + \mathrm{S}_0 \rightleftharpoons {}^1(\mathrm{TT}) \rightleftharpoons \mathrm{T}_1 + \mathrm{T}_1$$

To make the process exoergic, the singlet excitation energy has to be higher than twice the triplet excitation energy. Optimally the process should be close to be isoergic to have small energy losses and high singlet fission rates.
Additionally the recombination of the two generated triplets to another triplet exciton has to be suppressed. That can be achieved if the following two conditions are fulfilled.

$$\mathrm{E}(\mathrm{S}_1) \geq 2\ \mathrm{E}(\mathrm{T}_1)$$
$$\mathrm{E}(\mathrm{T}_2) > 2\ \mathrm{E}(\mathrm{T}_1)$$

Rather than singlet homofission, which takes place in the bulk of molecular crystals like pentacene and generates twice the same triplet exciton, this study focuses on singlet heterofission[3]. Here we discuss energy level matching and the aspect of coupling matrix elements for singlet heterofission.

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Quantum Chemical Microsolvation by Automated Solvent Placement

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Many chemical reactions take place in solvent and the chemically relevant solution-phase conformation of the reactant may differ significantly from its gas phase or solid-state conformation. To accurately account for their reactivity an explicit incorporation of solvent molecules may be required. This is in particular true for biomolecules and biochemical reactions, that take place in water. Defining the number of solvent molecules and its exact location is a great challenge. Thus, we developed a physics based approach to microsolvation, where we deduced the number and location of solvent molecules in an automated way based on the free energy solvation thermodynamics derived from Molecular Dynamics (MD) Simulations and Grid Inhomogeneous Solvation Theory (GIST). This enabled us to rigorously define the number and positions of individual solvent molecules for subsequent quantum chemical investigations, which is a prerequisite to study large bioinorganic structures and their reactivity that cannot be accessed by ab initio MD due to its size. We showcased the applicability of this computational protocol for a number of biologically relevant molecules, including urea, aspartate, and benzoic acid.[1]

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Fully numerical calculations on atoms and diatomic molecules

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Although fully numerical electronic structure calculations on atoms and diatomic molecules have a long history [1], running such calculations has traditionally required extensive effort and the available programs have been restricted to e.g. only restricted open-shell configurations, a low-order numerical approach (e.g. only cubic basis functions), and to few density functionals. I have recently developed a new program called HelFEM [2] that solves these issues. HelFEM employs a basis set composed of numerical shape functions for the radial part and spherical harmonics for the angular part, both in the case of atoms [3] and diatomic molecules [4], and yields fully variational energies. The approach used in HelFEM affords stable and fast convergence to the self-consistent field solution thanks to modern convergence accelerators, as well as to the basis set limit thanks to its support for high-order polynomial basis functions (15 by default) [3]. The fully numerical approach in HelFEM allows reproduction of accurate reference values for various systems or functionals of interest. In addition to strong electric fields [3,4], atoms and diatomic molecules can also be calculated in extremely strong magnetic fields [6], found e.g. in the atmospheres of white dwarfs and magnetars, which change not only the ground state geometry of a molecule, but also have significant effects on its ground spin state. At present, HelFEM supports non-relativistic calculations on atoms [3] as well as diatomic molecules [4] at the Hartree–Fock or density functional level of theory. Hundreds of local density approximation (LDA), generalized gradient approximation (GGA) and meta-GGA functionals are supported via an interface to libxc [5], also including global hybrid functionals such as B3LYP and TPSSh. Fully spin restricted, spin-restricted open-shell or unrestricted orbitals can be employed in calculations, which may be run using full molecular symmetry, partial symmetry, or no symmetry. The program is fully self-initializing, and can be started from e.g. the core guess or the superposition of atomic potentials (SAP) [7]; the program can also calculate the radial potentials needed for SAP.

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The molecular electric properties under the influence of spherical harmonic potential

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Among many potentials that can be used to model the effect of spatial confinement the harmonic oscillator potential is one of the most widely applied. It allows for the representation of chemical cages of different structure, especially the nanotube-like or fullerene-like ones. It is important to note that in the vast majority of works devoted to the studies of electric properties of spatially confined systems, the harmonic potential of cylindrical symmetry was applied [1-3]. Thus far, its spherical counterpart was used mainly to describe properties of spatially restricted atomic systems [4-5]. Therefore, our main goal was to analyze how the presence of the spherically symmetric harmonic oscillator potential affects the molecular electric properties and to characterize the impact of the relative position of the considered molecules and spherical confinement on these properties. Moreover, we made an attempt to assess the influence of the topology of confining environment on the dipole moment, polarizability and first hyperpolarizability, by comparing the results obtained in the spherical and cylindrical harmonic potential. The quantum-chemical calculations were carried out for three molecules with linear symmetry, i.e. LiH, LiF and HF. The conducted research demonstrated that the values of electric properties strongly depend on the relative position of the molecules and applied spherical harmonic potential. The trends of changes in the electric properties, caused by increasing the confinement strength, were found to vary quite significantly. Moreover, in the vast majority of cases, significant differences in the values of electric properties, obtained in the cylindrical and spherical confinement of a given strength, were observed [6].

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Nuclear Quantum Effects from the Analysis of Filtered Trajectories

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Nuclear quantum effects (NQEs) have significant contribution to thermodynamic quantities and structural properties, furthermore expensive methods are necessary for their accurate calculations such as path-integral molecular dynamics (PIMD)[1]. Because of this, in most calculations NQEs are simply neglected or only taken into account within the quantum harmonic oscillator approximation.
Herein we present a new method, Generalized Smoothed Trajectory Analysis (GSTA) to determine NQEs from molecular dynamics simulations. To obtain quantum corrected data the time dependent variables of simulations such as coordinates, forces and velocities are filtered with a kernel function derived from the partition function of the harmonic oscillator. GSTA gives the exact zero point energy for harmonic oscillator, and also leads to the correct heat capacities in the high temperature limit, even for anharmonic systems. One of the main advantage of GSTA is that the different motions, like rotation, translation, vibration etc., do not need to be separated. As a post-processing analysis of classical simulations, our technique can be paralleled with the two-phase thermodynamic (2PT) method[2], but the expected field of application can be similar to that of the PIMD simulations.

The broad applicability is demonstrated on examples of harmonic oscillator and different states of water. Born-Oppenheimer Molecular Dynamics (BOMD) simulations have been performed for ideal gas at B3PW91/6-311g(d,p) level of theory up to the temperature of 5000 K.
Classical molecular dynamics have been carried out with SPC/Fw water model for Ih ice, liquid water and vapor. Respect to the experimental heat capacity, GSTA outperforms previous calculations from the literature in a very wide temperature range at much smaller computational cost than PIMD. Nuclear quantum effects on the structure of liquid water are also reproduced (Figure 1).

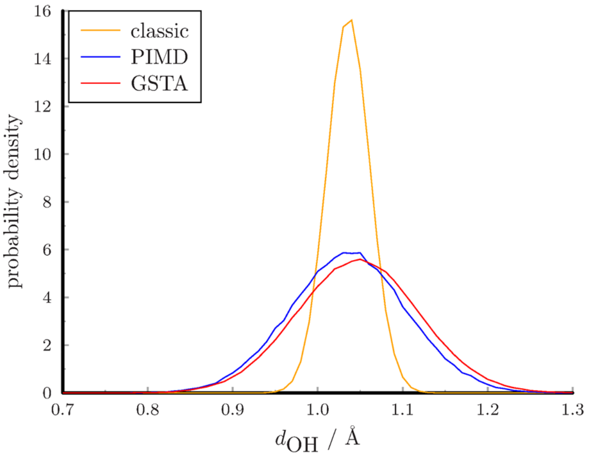

Figure 1: probability distribution functions of intramolecular O-H distance.

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Excited states in QMC: Which wave function? Which variational principle?

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We investigate here the general key ingredients needed to efficiently achieve reliable excitation energies in quantum Monte Carlo. For the small and yet challenging cyanine dyes and retinal models, we show that the use of selected configuration-interaction expansions (CIPSI) leads to compact Jastrow-Slater wave functions and a balanced description of both the ground and excited states. Furthermore, we analyze the use of different variational principles for the minimization of the wave functions in quantum Monte Carlo. In particular, we compare the performance of state-specific variance minimization and of state-average energy minimization. For this purpose, we use a revised version of the Newton minimization method in which the exact expression of the Hessian is manipulated to obtain a faster and more stable convergence.

Vanadium Tetrasulfide Nanowires: half-metal antiferromagnetic semiconductor with Carrier Doping towards antiferromagnetic spintronics

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Abstract

Antiferromagnetic (AFM) spin devices could be one of the representative components for spintronic applications because of many advantages, resistance to magnetic field perturbation, stray field-free operation, and ultrahigh device operation speed. However, detecting and manipulating the spin in AFM materials is still a challenge because of the absence of a net magnetic moment and spin degeneracy in the band structure. Engineering the electronic and magnetic structures of material systems enables the novel exploration of new physical properties, which could be promising solutions to these problems. We discovered three phases of vanadium tetrasulfide nanowires (VS_4) which are AFM. Results indicate that gate voltage can manipulate the spin orientation of VS_4 leading to a transition from AFM to half-metal antiferromagnets (Figure 1). It means that we can manipulate the orientation of spin currents by using different gate voltages. This opens a new strategy towards AFM spintronics for expanding applications of the spin field effect transistor in one dimensional nanowires.

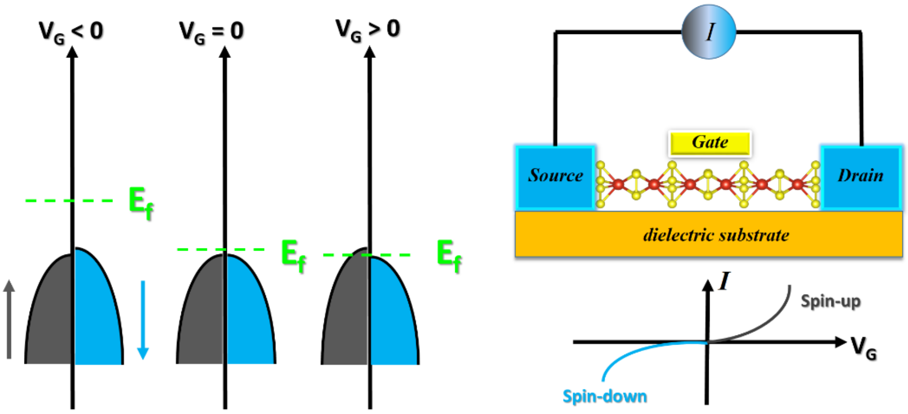

Figure 1: Diagram of manipulation of the spin orientation by the gate voltage

A Variational Approach to London Dispersion Interactions Without Density Distortion

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London dispersion interactions play a crucial role in physical, chemical and biological processes. Despite their nature being elucidated already in the 1930s, calculating accurately the strength of these interactions remains a computational challenge and is one of the main challenges for Density Functional Theory (DFT) today. In our work [1] we have introduced a class of variational wavefunctions that capture the long-range interaction between systems (atoms and molecules) without changing the diagonal of the density matrix of each monomer. As the individual monomer densities are kept fixed, we can also unambiguously assess the effect of the density distortion on London dispersion interactions: for example, we obtain virtually exact dispersion coefficients between two hydrogen atoms up to C_{10}, and relative errors below 0.2% in other simple cases. We are now assessing the method for larger systems and studying the effect of using different approximations for the monomers.

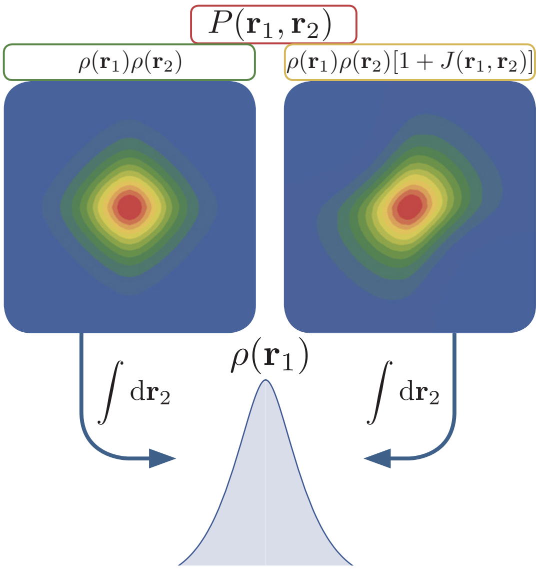

Figure 1: illustration of the basic principle used in the paper: the intermonomer pair density can be distorted to produce attraction, while keeping the individual monomer densities constant.

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Poster: P2-36

Relativistic and Dynamic effects in Computational ^{1}H-NMR Spectroscopy of Iridium Polyhydride complexes

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In the field of transition-metal complexes, the accurate calculation of NMR parameters is a challenging task and requires elaborate computational models. Several factors, such as relativity and dynamics, can significantly alter the NMR chemical shift values. For instance, there is evidence demonstrating that conformational dynamics is essential for a proper determination of the NMR chemical shifts in various transition-metal complexes.[1]

Transition-metal hydride complexes often play an important role as transfer hydrogenation catalysts. Recently, various iridium deactivation products formed in the catalytic dehydrogenation of glycerol have been analyzed by experimental and computational approaches.[2] A point of special interest, the hydride positions, could not be established in the X-ray studies, however, because of their proximity to the heavy metal atoms.[3]

In this regard, we have established a computational protocol for the rational calculation of ^{1}H-NMR chemical shifts for the iridium polyhydride $[Ir_6(IMe)_8(CO)2H_{14}]^{2+}$ complex (see Figure 1) to validate the assignments previously made. In particular, the hydride resonances were investigated by static and dynamic ^{1}H-NMR chemical shift calculations, using a full four-component relativistic method and in conjunction with *ab-initio* molecular dynamics simulations to describe the relativistic effects and conformational dynamics, respectively.

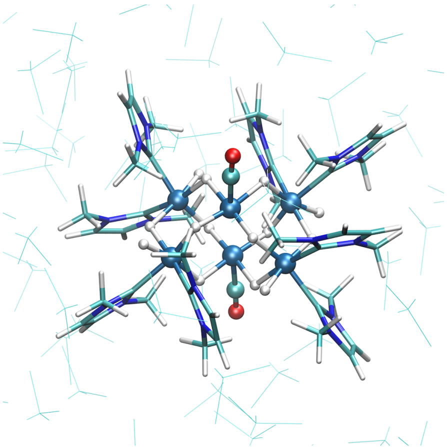

Figure 1: $[Ir_6(IMe)_8(CO)2H_{14}]^{2+}$ complex

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Ring Coupled Cluster Doubles at the Multireference Level

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Ring approximation within the internally contracted multireference (MR) coupled cluster (CC) framework of Mukherjee et al.[1] is worked out and tested. Derivation of the equations is based on generalized normal ordering and applies the corresponding generalized Wick-theorem. Contractions among cluster operators is avoided by adopting a normal ordered exponential Ansatz.

The MR ring CCD (MR rCCD) amplitude equations[2] show kinship, but are not equivalent with the extended random phase approximation (ERPA) based energy correction scheme, put forward by Pernal[3]. Original version of MR rCCD equations are presently amended with proper treatment of redundancy among double excitations. In the original formulation, huge number of cumulant contractions has been cut back by (i) the ring approximation and by (ii) restricting maximal cumulant rank at two. We find the latter approximation inappropriate. Equations are presently expanded with terms involving cumulants up to rank four.

Application of a generalized valence bond type reference function ensures a fragment structure of cumulants: nonzero elements appear with all indices assigned to the same bond. As a consequence, cumulant involving terms remain less expensive than their solely pair-contracted counterpart.

As compared with ERPA based energy correction, the advantage of MR rCCD lies with the availability of the wavefunction and its potential to abandon the need of filtering excitations allowed to enter the Ansatz.

Pilot applications are presented for torsional potentials and on examples of covalent bond breaking.

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Probing Ultrafast Photodynamics in Malonaldehyde with Transient X-Ray Absorption

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Excited-state hydrogen transfer is a fundamental chemical reaction of relevance throughout chemistry and biology. Malonaldehyde (MA) is the simplest example that exhibits both ground- and excited-state intramolecular H-transfer and is the functional unit of the family of *β*-diketones. Experimental investigations of its photodynamics are limited in number and scope due to the challenges related to resolving ultrafast timescales of hydrogen transfer and non-adiabatic processes in a symmetric system as well as the instability of MA at ambient temperatures.

Here, we perform an *in silico* transient X-ray absorption spectroscopy experiment at complementary carbon and oxygen *K*-edges to probe its potential to monitor the ultrafast internal conversion dynamics in MA upon excitation to the $S_2(\pi\pi^*)$ state. This is accomplished by combining *Ab Initio* Multiple Spawning[1] simulations with property calculations at the algebraic-diagrammatic construction for the polarization propagator level.[2] Our simulations show the sensitivity of the oxygen *K*-edge to fingerprint the ultrafast population transfer to the $S_1(n\pi^*)$ state through the H-transfer intersection, the concomitant dynamics along the bond-length alternation coordinate and the subsequent re-population of the ground state. Given the coming advances in X-ray light sources, our study proposes an experimental route to disentangle photodecay pathways in MA.

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MC–srDFT triplet response

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Density functional theory (DFT) is one of the most widely used methods in the field of computational chemistry. However, DFT is only reliable when considering systems that are dominated by a single determinant. Molecules including transition metals are often unsatisfactorily described by single determinant methods, and thus need multi-configurational (MC) methods. Such state-of-the-art MC methods that includes both static and dynamic correlation, e.g. CASPT2 and NEVPT2, are often very computationally expensive.

As a promising alternative the dynamic correlation from DFT is combined with the static correlation from CASSCF in the framework of short-range DFT, giving the name MC–srDFT. In the short-range DFT framework the two electron operator is split into a short-range and a long-range contribution to avoid double counting of the electron interaction, and to make the method fully variational.

$$\frac{1}{r} \rightarrow \frac{f(\mu)}{r} + \frac{1 - f(\mu)}{r} \tag{1}$$

Due to the variational formulation of MC–srDFT, response theory is straightforwardly applicable to the model. Following the singlet response work of Fromager et. al.[1], we have extended MC–srDFT with triplet response from a singlet reference wave function. Due to the way the MC–srDFT model is constructed, the Hessian contribution to the response equation is a sum of the long-range and short-range contributions.

$$\left(\boldsymbol{E}^{[2],\mu} - \omega \boldsymbol{S}^{[2],\mu}\right) \Lambda(\omega) = i\boldsymbol{V}_x^{[1],\mu}, \qquad \boldsymbol{E}^{[2],\mu} = \boldsymbol{E}^{[2],\mathrm{lr}} + \boldsymbol{E}^{[2],\mathrm{sr}} \tag{2}$$

Furthermore, in an effort to improve the accuracy of the short-range functionals our implementation of the MC–srDFT model has been extended to include meta-GGAs. Meta-GGAs should in principle provide a more accurate short-range description, compared to srGGA and srLDA. This development has been utilizing the srTPPS meta-GGA from Goll et. al.[2]

The new code has been implemented in a development version of DALTON.

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Theoretical Prediction of Resonance Raman and Resonance Raman Optical Activity Spectra

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Raman optical activity (ROA), the difference in Raman scattering intensity for left and right circularly polarized light, is a powerful tool for studying chiral molecules and determining the structure of biomolecules in their native environment. Raman optical activity spectra obtained from *ab initio* quantum chemical calculations, using the far-from-resonance approximation (FFR), can often enhance the interpretation of the experimental spectra. The FFR approximation is, however, no longer valid when the incident laser frequency becomes close to the energy of an electronic excited state.

We present a fully analytic derivative extension of a method, first introduced by Jensen and co-workers [1], to compute the resonance vibrational Raman (RR) and Raman optical activity (RROA) of molecules using density functional theory. In this approach, an imaginary empirical damping parameter, corresponding to an effective inverse lifetime of the excited states, is added to the incident frequency. The formalism is the same as the FFR case except the frequency-dependent mixed polarizability tensors and their respective geometric derivatives become complex. The additional work required to handle the complex case increases the computational cost by less than a factor of two. Additionally, this approach is compatible with the two-step procedure in which the force field and Raman/ROA tensors are computed in separate steps, thus allowing for the use of different levels of theory for each step [2].

Preliminary results suggest that this approximate method recovers a significant amount of the resonance effects as the incident frequency approaches an electronic excitation and compares well with vibronic methods when the excited state geometry is similar to the ground state geometry. In the case of a strong resonance with a single electronic state, the calculated RROA obtained using this method is monosignate with the same relative intensities as the parent Raman spectrum, as predicted and observed by Nafie [3-4].

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Modeling Localised Excitations and Electron Transfer with a Non-orthogonal Product Wave Function Approach

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The description of intermolecular transfer of electrons and electronic excitations is an important part of the theoretical investigation of molecular electronics. It requires models that allow accurate predictions and facilitate understanding of the underlying processes. For this purpose we employ a non-orthogonal product wave function approach, along with a Löwdin orthogonalization procedure[1], to obtain electronic coupling coefficients of multi-state systems.

The use of non-orthogonal wave functions has found renewed interest in, e.g. non-orthogonal configuration interaction (see for example [2]), and it has been applied in the calculation of electronic coupling coefficients at different levels of theory (e.g. [3], [4]). Here, we present our computational approach based on antisymmetrised products of individually selected determinants of the building blocks of the actual, extended system. We compare its performance to other approaches and apply it to singlet fission and the intermolecular transfer of electronic excitations.

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Approaching CCSD(T)/CBS energies for molecules of up to 1000 atoms: method development and benchmark applications

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Recent optimization efforts [1-3] and extensive benchmark applications [4-5] are presented illustrating the accuracy and efficiency of the local natural orbital (LNO) coupled-cluster (CC) with single-, double,- and perturbative triple excitations [LNO-CCSD(T)] method.

The accuracy of the local approximations can be systematically improved via a single parameter in a black box manner. The complete basis set (CBS) limit of LNO-CCSD(T) is reliably approached by extrapolating from augmented triple- and quadruple-zeta basis sets [CBS(T/Q)], since the quasi-linear dependence of the AO basis emerging in large molecules is also handled. [4]

Compared to canonical CCSD(T) references computed for molecules of up to 63 atoms the average LNO-CCSD(T) correlation and reaction energy errors with Normal settings are below 0.07% and 0.34 kcal/mol, respectively. [1] The same errors drop down by a factor of 3 when using the Tight truncation thresholds.[4] Further benchmarking performed on systems of 60-130 atoms revealed systematic convergence with Loose, Normal, Tight, etc. truncation thresholds, which can also be exploited to determine error estimates with respect to CCSD(T). Even for particularly complicated cases with up to about 100 atoms LNO-CCSD(T)/CBS(T,Q) results agree within 1-2 kJ/mol with recent, explicitly correlated local CCSD(T) reaction and interaction energies. [4]

An LNO-CCSD(T)/CBS(T,Q) energy evaluation usually takes less than an order of magnitude more time than DF-HF/CBS(T,Q), even in the range of a few hundred atoms. Parallel execution can further decrease wall times to the range of hours. Thus LNO-CCSD(T)/CBS(T,Q) is not the rate limiting if applied in computational protocols involving geometry optimization or frequency evaluation with DFAs above rung three. The low minimal memory requirement (few tens of GBs) and the negligible disk use of the method makes it routinely applicable for the majority of closed-shell molecules appearing in modern chemistry even with easily accessible, single CPU workstations.

The capabilities of the current LNO-CCSD(T) implementation are demonstrated on large, three-dimensional examples, such as protein-ligand binding.[5] An LNO-CCSD(T)/CBS(T,Q) correlation energy calculation is feasible for more than 1000 atoms and almost 50000 atomic orbitals using an 8-core processor and 120 GB memory (see Figure.).

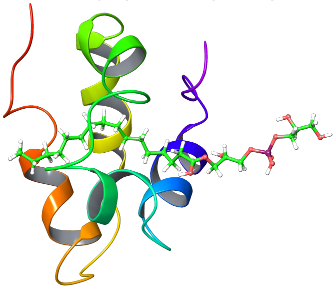

Figure 1: Lipid transfer protein, 1023 atoms,
LNO-CCSD(T)/def2-QZVPPD (49656 AOs) takes ~ 4 weeks on 8 cores.

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Photoinduced Electron Injection and Charge Separation in a Dye-sensitized Photoanode: A Quantum-classical Semiempirical description

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Increasing energy demand, environmental concerns and rising CO_2 levels demonstrate the need to transition from a fossil to renewable fuel and energy economy. Direct conversion of solar energy to high energy molecular fuels would facilitate such a transition. Promising devices for the conversion of visible light directly into molecular fuel are Dye-Sensitized Photoelectrochemical Cells (DSPECs), which have attracted much interest in recent years [1]. To fulfil the potential of DSPECs in producing clean photosynthetic fuels, more effort is required to increase their chemical stability and efficiency. Since the efficiency of these devices is closely linked to the crucial process of photoinduced charge separation and charge recombination, molecular components and interfaces need to feature optimal energy level alignement. Computational studies can provide insight into these fundamental processes and suggest design principles. However, given the complexity of the system, a good compromise between accuracy and computational cost has to be found. Here, we use a combination of Density Functional based Tight Binding (DFTB) [2,3] and an extended Hückel approach [4] to model photoinduced charge separation and electron injection from organic dyes into a TiO_2 electrode.

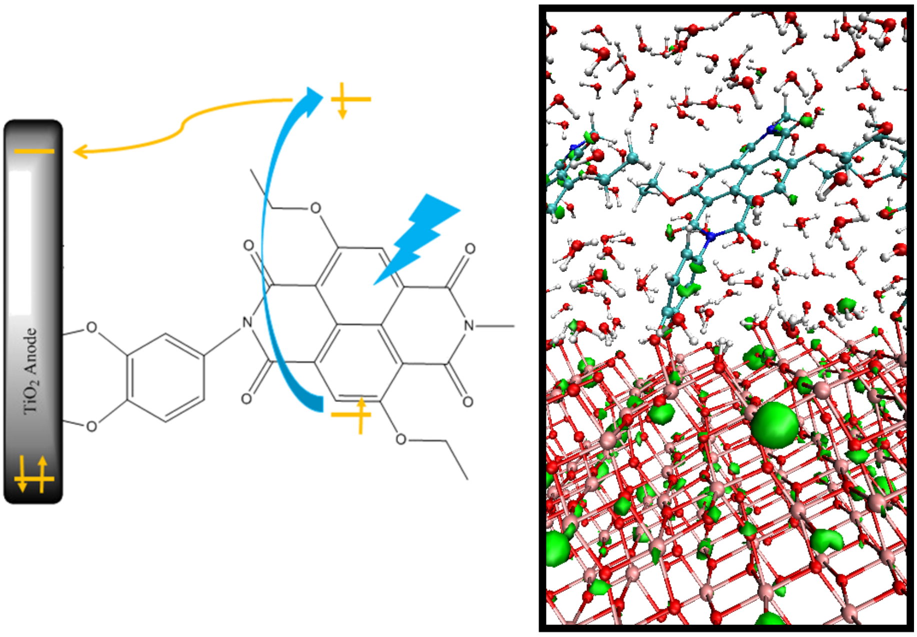

Figure 1: Electron injection from a photoexcited dye into a TiO_2-electrode

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Differential Many-Body Cooperativity and Characterisation of Cu(I) TADF Complexes

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The differential many-body expansion [1] is applied to investigate non-additive and cooperative effects in UV/Vis spectra, singlet-triplet energy gaps and electronic energies of Cu(I) and Ag(I) halide TADF complexes. The dependence of these properties on different ligand systems is studied in terms of diphenylphosphinopyridine-type ligand system with and without halide containing arylphosphines [2,3], see Figure 1. Subsystems for the differential many-body expansion are obtained by substituting metals and halides. Properties of subsystems are described by first-order terms while second-order terms describe non-additive but pairwise contributions, and third-order - and higher-order - terms can be understood as indicator for cooperativity.

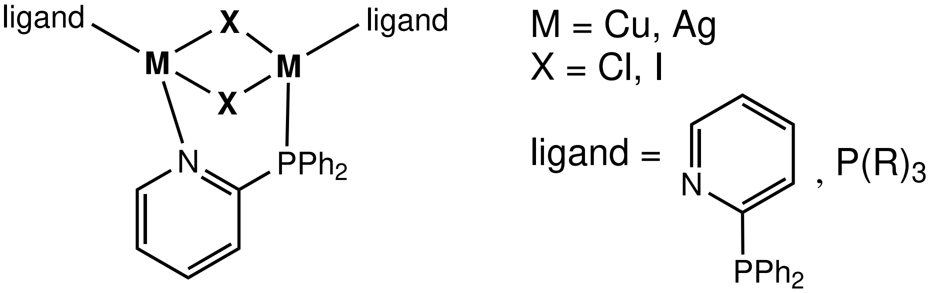

Figure 1: *Schematic structure of the complexes studied.*

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Atomistic origins of the preferential stabilization of perovskite over non-perovskite phases of mixed cation lead halide perovskites

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Mixed cation lead halide perovskites have attracted wide attention due to the possibility of preferentially stabilizing the perovskite phase with respect to photovoltaically less suitable competing phases.[1-2] In this work, through a theoretical analysis, we study the phase stability of binary $HC(NH_2)_2^+$ (FA^+)-rich[1] and Cs^+-rich FA/Cs and $CH_6N_3^+$ (GUA)/FA mixtures as well as ternary Cs/GUA/FA mixtures. Our study yields a series of design principles for the fabrication of stable lead halide perovskites with mixtures of monovalent cations.
Calculations of FA^+-rich $Cs_xFA_{(1-x)}PbI_3$ ($0<x<0.5$),[1] suggest that if the structural characteristics of the non-perovskite δ phases of the pure compounds differ significantly, mixing is energetically favoring the perovskite over the non-perovskite phase. However, despite the significant differences in the δ phases of $FAPbI_3$ and $CsPbI_3$, in Cs^+-rich $FA_xCs_{(1-x)}PbI_3$ ($0<x<0.5$) mixtures, stable perovskite phases cannot be formed. This contrasting finding leads us to consider not only the structural differences between the non-perovskite phases of the pure compounds but also the volume difference between their perovskite phases. Indeed, mixing in the perovskite phase is getting unfavorable upon incorporation of a large cation into a relatively small lattice.
Although mixing of FA/GUA is possible, it is not sufficient to stabilize the perovskite phase at room temperature. Probing the possible stabilization in ternary Cs/GUA/FA mixtures, instead we conclude that stable mixtures that contain 17% of Cs^+ and GUA up to 33% can be formed. This finding reveals a third design principle, according to which mixing monovalent cations that would be per set outside the stability range with other cations that can compensate the size, so that the average radii of the mixed cations lies within the suitable Goldschmidt tolerance range[3] can lead to the formation of ternary perovskite mixtures with enhanced stability.
Our investigations on the potential preferential stabilization of the perovskite phase upon mixing is complemented by band gap calculations of the mixtures that show that the stable perovskite phases of binary FA^+-rich FA/Cs and of the ternary Cs/GUA/FA mixtures can be potential candidates for single-junction solar cell applications. In addition, if the perovskite phase of Cs^+-rich Cs/FA mixtures could be kinetically trapped it would be a potential candidate for tandem solar cell applications. In such a way, our suggested design principles pave the way for the preparation of mixed cation lead halide perovskites with enhanced stability and optical properties.

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Prediction of properties for sizable molecular systems including spin-orbit effects

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We will present our efforts to expand the usability of the quasirelativistic two-component (2c) GW/(c)BSE and hybrid time-dependent(TD)-DFT methods to calculate properties of large molecules containing heavy elements [1]. For the properties of these compounds spin-orbit effect can often not be neglected if a quantitative description is sought for. To efficiently obtain results from GW/(c)BSE [2] highly optimized 2c contour-deformation (CD) and analytic-continuation (AC) GW methods within the resolution-of-the-identity approximation (RI) are used, allowing us to compute properties for sizable systems at local compute nodes also for extended sets of molecules. For 2c hybrid TD-DFT RI-K and seminumerical algorithms for exchange were implemented, allowing to obtain spin-orbit dependent properties of molecules with hundreds of atoms. Further the two-component extension of the current-dependent metaGGA response [3] formalism was implemented. This is crucial to describe antiferromagnetic coupled systems or current-carrying states, where the current is induced by spin-orbit coupling itself or external fields, e.g. magnetic fields. Finally, a tool converting theoretical and experimental spectra to common variables known by workers in both fields (e.g. RGB colour codes) was implemented within the TURBOMOLE program package to allow for a rapid comparison between experimental and theoretical data. Due to the combined efficiency and robustness of the developed algorithms many possible molecular candidates containing heavy elements can be screened on locally available compute nodes, e.g. helping to identify the molecular structure of compounds where other standard methods as X-ray crystallography cannot readily be used.

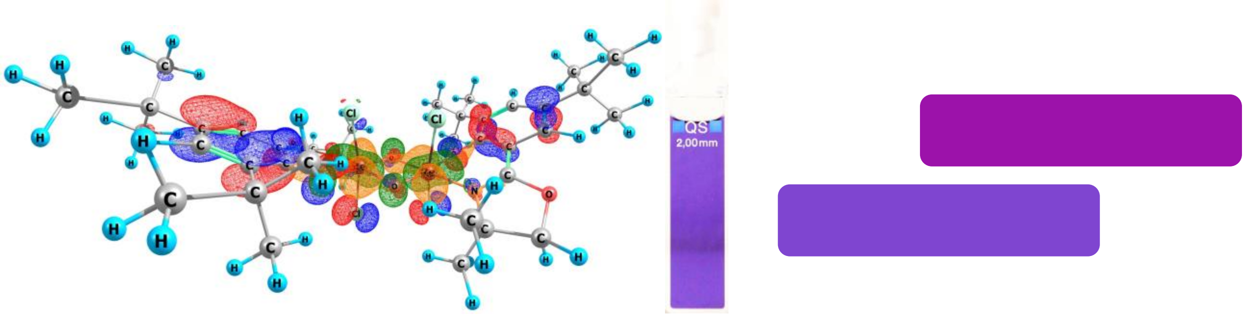

Figure 1: left: trial molecule, middle: picture of measured sample, upper right: calculated color (2c GW/cBSE@PBE0) from a possible trial compound, lower right: measured color from sample compound.

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Compact numerical solutions to the two-dimensional repulsive Hubbard model obtained via non-unitary similarity transformations

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Similarity transformation of the Hubbard Hamiltonian using a Gutzwiller correlator leads to a non-Hermitian effective Hamiltonian [1], which can be expressed exactly in momentum-space representation, and contains three-body interactions [2]. We apply this methodology to study the two-dimensional Hubbard model with repulsive interactions near half-filling in the intermediate interaction strength regime ($U/t = 4$).

We show that at optimal or near optimal strength of the Gutzwiller correlator, the similarity transformed Hamiltonian has extremely compact right eigenvectors, which can be sampled to high accuracy using the Full Configuration Interaction Quantum Monte Carlo (FCIQMC) method [3], and its initiator approximation.

Near-optimal correlators can be obtained using a simple projective equation, thus obviating the need for a numerical optimisation of the correlator. The FCIQMC method, as a projective technique, is well-suited for such non-Hermitian problems, and its stochastic nature can handle the 3-body interactions exactly without undue increase in computational cost. The highly compact nature of the right eigenvectors means that the initiator approximation in FCIQMC is not severe, and that large lattices can be simulated, well beyond the reach of the method applied to the original Hubbard Hamiltonian. Results are provided in lattice sizes upto 50 sites and compared to auxiliary-field QMC.

New benchmark results are provided in the off half-filling regime, with no severe sign-problem being encountered. In addition, we show that methodology can be used to calculate excited states of the Hubbard model and lay the groundwork for the calculation of observables other than the energy.

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Magnetically-induced current density investigation in carbohelicenes and azahelicenes

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In this poster, we investigate the magnetically-induced current (MIC) density for a variety of ortho fused polycyclic aromatic molecules at the density functional theory level with the gauge including magnetically induced current (GIMIC) method (Figure 1). With this method, the aromatic character of each ring in a homologous series of carbohelicenes with an increasing number of fused benzene rings is assessed and compared with other aromaticity criteria such as Nucleus Independent Chemical Shifts [NICS(0), $\text{NICS}_{zz}(0)$] and Bond Length Alternation (BLA) parameters. All criteria indicate that the two outer rings are the most aromatic ones [*i.e.* higher induced current, more negative NICS(0) and $\text{NICS}_{zz}(0)$ values, and smaller BLA values]. For the large helicenes ($n > 10$), the current drops along the following four rings and then rise again. Additionally, we have proven that this behavior is not due to a difference of the local magnetic field coming from a difference of orientation of the ring with respect to the external magnetic field (oriented along the helical axis). Upon fusing additional benzene rings to form the hexa-peri-hexabenzo[7]helicene, some rings (B, D, and F) are a lot less aromatic (even non-aromatic) than the others. The NICS(0) and $\text{NICS}_{zz}(0)$ values exaggerate this behavior because they are all positive values, which is a signature of antiaromaticity. Then, when substituting one, three, or four benzene rings by pyrrole ones to form the mono-aza-[7]-helicene, the tri-aza-[7]-helicene, and the tetra-aza-[7]-helicene, remarkable changes in the electronic structures of helicenes are observed. Indeed, the induced currents are always smaller in the pyrrole rings than in the benzene ones.

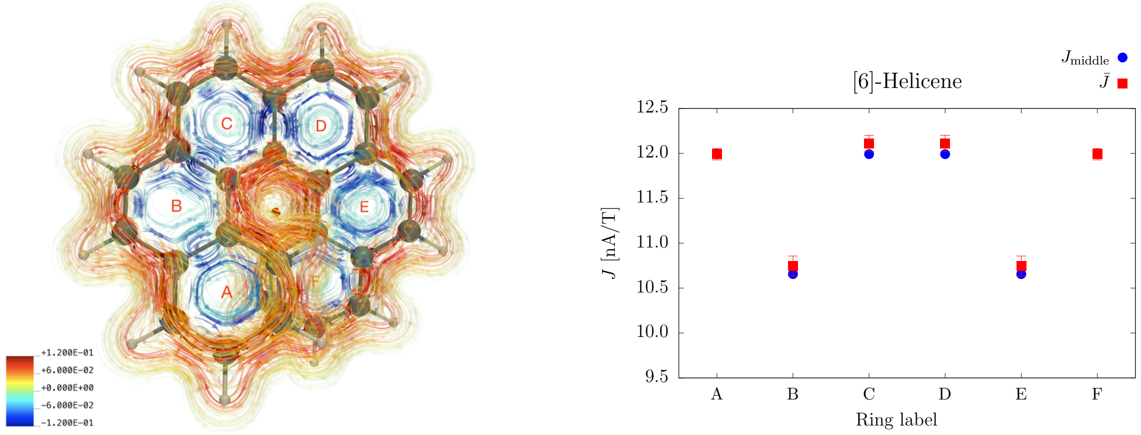

Figure 1: 3D Streamline plot of the current density (left) and total induced current (right) for [6]-helicene molecules.

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Spectroscopy with RT-TDDFT

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Time dependent density functional theory (TDDFT) is the work horse of theoretical spectroscopy due to its reasonable compromise between accuracy and computational cost. Complementary to linear response TDDFT (LR-TDDFT), like Sternheimer's or Casida's approach, a direct numerical integration of the time dependent Kohn-Sham equations is also viable for the calculation of spectroscopic properties. Distinct features of the real time TDDFT (RT-TDDFT) approach are an advantageous scaling for larger molecules, response beyond the standard linear response and the complete spectral range from just one simulation run.

Since the electronic response of the system to a perturbation is tracked in real time, a range of linear response functions can be calculated straightforwardly, giving access to purely electronic responses, such as UV/VIS and Xray absorption spectra, as well as electro-magnetic responses, such as electronic circular dichroism (ECD) spectra. These applications of RT-TDDFT are discussed with respect to gauge invariance and origin dependence also in the presence of non-local potentials [1].

Moreover RT-TDDFT has been be extended to the calculation of Raman spectra [2] in a short time approximation, using a Placzek type expansion of the electric-dipole electric-dipole polarizability [3,4]. This approach allows the simulation of full excitation profiles, including non-resonance as well as resonance Raman spectra [5]. In the resonance case Heller's excited state gradient approximation [6] is recovered from the RT-TDDFT calculations using Padé approximants [7].

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Embedding Schemes Applied to Strongly Correlated Systems

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Two different embedding schemes are presented to study strongly correlated systems. In the first approach, an embedded FCI (full Configuration Interaction) is performed on top of the Distinguishable Cluster approximation (DCSD) [1]. In order to analyse the accuracy of this metod, a uniform dissociation of a 1D H-chain is studied. The latter still represents a difficult case for conventional methods [2]. In the second, a CEPA (Coupled-electron pair approximation) [3, 4] approach embedded in CISD (CI method with single and double excitations) is accomplished in order to investigate size-inconsistency issues in different open-shell transition metals. These systems are still an open question when based on the accuracy of a single-reference method.

Hydrogen systems For this we calculate two corrections: a basis set correction from explicitly correlated DCSD, and a correlation correction from an embedded FCI calculation on specific orbitals. These corrections, when applied on top of the DCSD calculations, give a good match with AFQMC+DMRG data by Motta et al. [2]. Further, uniform dissociation of 2 and 3 dimensional H-systems were also investigated. In all cases of dissociation the energy converges to the correct limit of separated Hydrogen atoms.

CEPA embedded in CISD The CEPA embedding in truncated CI method gives the possibility to study the effect of the excitation energies arising from the non-size-extensivity errors. The results of our calculations for three different compounds containing Cu^{2+} agree well with the conclusions from Giner et al. [5]. Embedding CISD in CEPA can be used to improve CEPA in bond-breaking situations.

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$|\Psi|^2$ Analysis: Extracting Valence Bond Information from Arbitrary Wave Functions

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In the last decades, valence bond (VB) theory regained popularity due to the insight it offers into the nature of bonding in molecules. Since it describes resonance between Lewis structures, its results are often intuitively understandable for chemists. However, VB calculations are less computationally efficient than those of other methods and need theoretical preparation, which can add bias.

The $|\Psi|^2$ analysis is also connected to the Lewis picture of chemical bonding [1]. It can be applied to any wave function and gives information about the most probable electron arrangements, i.e. local maxima of $|\Psi|^2$ that partition $\mathbb{R}^{3N}$ into their basins of attraction. In many cases, these maxima resemble VB structures. A weight can be assigned to each maximum by Monte Carlo integration of its basin.

Ideally, both of these methods should give agreeing results. This is put to the proof in the present work: $|\Psi|^2$ weights of maxima are compared to Chirgwin-Coulson, Löwdin, and inverse weights of VB structures.
Furthermore, the transferability of this VB structure weight extraction to arbitrary wave functions is proven by application to complete active space (CAS), Jastrow-CAS, and Jastrow-VB wave functions.

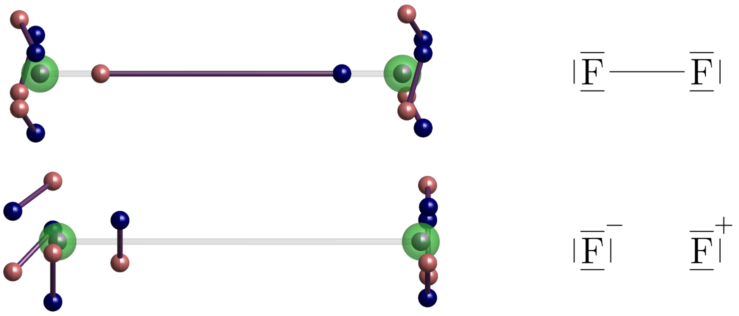

Figure 1: covalent and ionic $|\Psi|^2$ maxima of a Jastrow-CAS wave function (left) resemble the respective VB structures (right) of fluorine.

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Combined DFT and spectroscopic study of biologically active Cu-, Ni-, Co-Quinolone complexes with phenantroline

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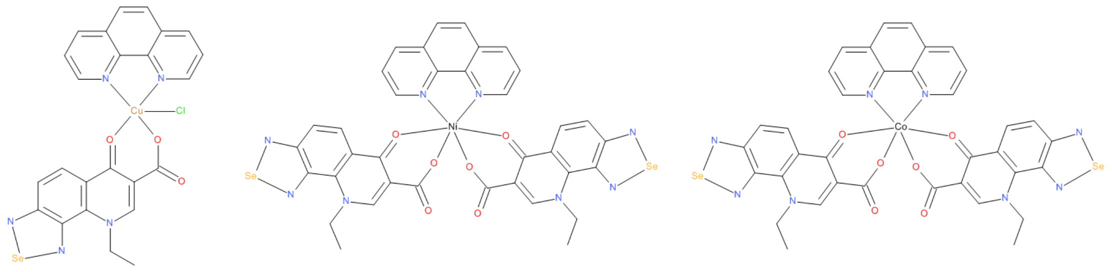
Quinolones are generally used against many gram positive and gram negative bacteria.[1] It has been shown that the presence of selenium in the quinolone structure can positively affect its biological impact.[2] Newly synthesized [3] biologically active copper (**1**), nickel (**2**), and cobalt (**3**) complexes with selenadiazoloquinolone ligands have been studied by theoretical calculations and in situ EPR/UV-vis-NIR spectroelectrochemistry. Structure of these complexes is shown in Figure 1. Due to the complicated structure of coordination polyhedron (*i.e.* three bidentate ligands in the case of **2** and **3**) a considerable attention has been paid to the conformation analysis of the studied systems. Calculated results were compared with the experimentally obtained X-ray geometries. Non-relativistic Fermi contact terms as well as relativistic hyperfine coupling constants and g-tensors are presented and compared with in situ EPR experiment.



1 **2** **3**

Figure 1: Structure of systems under study.

Acknowledgement

We are grateful to the Slovak Grant Agencies APVV (contracts No. APVV-15-0079 and APVV-15-0053), VEGA (contracts No. 1/0598/16, 1/0416/17 and 1/0466/18) and SIVVP project (ITMS code 26230120002). To all financing sources the authors are greatly indebted.

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Efficient Implementation of NMR Coupling Tensor Calculations

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Nuclear spin-spin coupling constants are a quantity frequently measured in organic and inorganic chemistry for structure analysis. Quantum chemically, they are calculated as the second derivative of the energy w.r.t. the magnetic moments of the coupling nuclei. According to Ramsey's theory [1,2], four terms arise, labeled Fermi-contact (FC), spin–dipole (SD), paramagnetic spin–orbit (PSO) and diamagnetic spin–orbit (DSO). The first three terms require the iterative solving of response equations, whereas the DSO term is an expectation value over the ground state density. These terms, including the FC/SD cross term needed for anisotropic couplings, have been implemented into the program package TURBOMOLE.

Coupling constants in molecules with about 100 atoms can routinely be calculated within a few hours. Molecules with 1000 atoms are in range if one preselects certain atoms and/or employs the resolution of the identity for K (RI-K) or the seminumerical evaluation of the exchange, both of which are favorable for larger basis sets. In addition, OpenMP parallelization is available.

A further reduction of computational cost can be achieved by choosing smaller basis sets for atoms not directly involved in the couplings of interest. Findings on which atoms can be excluded are presented.

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Is the Excited State Aromaticity a Driving Force for Planarization of Dibenzannelated 8π-Electron heterocycles?

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Excited state aromaticity (ESA), as given by Baird's rule, can be a driving force for changes in excited state structures and other properties, such as observed for dibenzo[*b,f*]oxepin (Figure 1a).[1,2] Dibenzannelated heterocycles with central 8π-electrons ring, found in a range of applications such as in antipsychotic drugs and photofunctional materials, often adopt a bent structure in the ground state (S_0) but can become planar in the first excited states (S_1 and T_1), fulfilling the requirements for excited state aromaticity.[3] Herein we report a quantum chemical investigation focused on how the position, type and number of heteroatoms in the central 8π-electron ring can affect the S_1 and T_1 states of a range of dibenzannelated heterocycles (Figure 1b) and to extent aromaticity.[4] For molecules with one or two heteroatoms in the central ring, their optimal S_1 and T_1 structures are (nearly) planar and have $\pi\pi^*$ character, being influenced by ESA to a significant degree. Moreover, the effect is much stronger for molecules containing nitrogen while it is weaker for oxygen-based compounds, following the established aromaticity trend of the electronic ground state. On the other hand, compounds with N=N bonds are strongly puckered in the excited state as consequence of their nonaromatic $n\pi^*$ excited state.

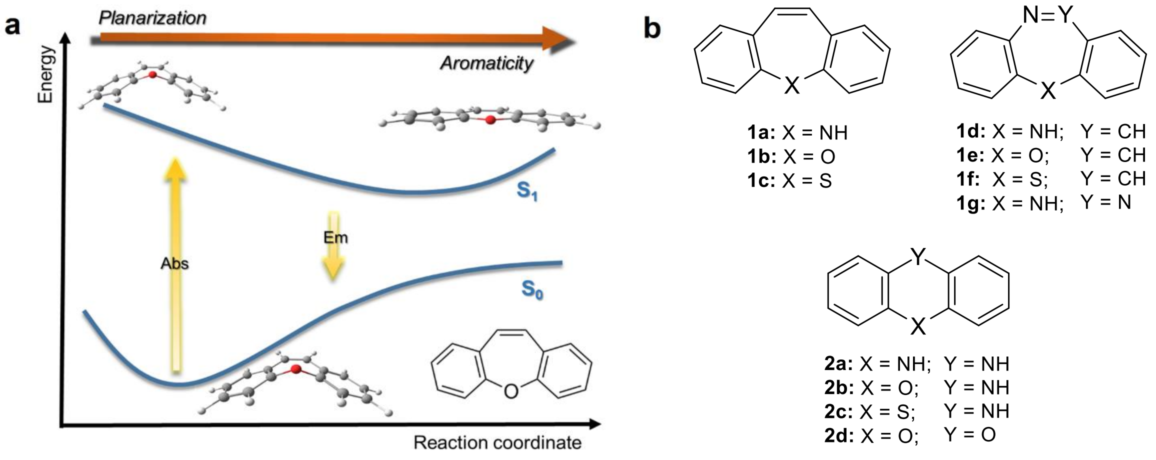

Figure 1: a) Schematic representation of the potential energy surfaces for planarization of dibenzo[b,f]oxepin in the S_1 state. b) Molecules investigated in this work.

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An efficient first principles method for molecular pump-probe NEXAFS spectra: Application to thymine and azobenzene

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Pump-probe near edge X-ray absorption fine structure (PP-NEXAFS) spectra of molecules offer insight into valence-excited states, even if optically dark. In PP-NEXAFS spectroscopy, the molecule is "pumped" by UV or visible light enforcing a valence excitation, followed by an X-ray "probe" exciting core electrons into (now) partially empty valence orbitals. Calculations of PP-NEXAFS have so far been done by costly, correlated wavefunction methods which are not easily applicable to medium-sized or large molecules. Here we propose an efficient, *first principles* method based on density functional theory in combination with the transition potential and ΔSCF methodology (TP-DFT/ΔSCF), to compute molecular ground state and PP-NEXAFS spectra. We apply the method to $n \rightarrow \pi^*$ pump / O-K-edge NEXAFS probe spectroscopy of thymine (for which both experimental and other theoretical data exist), and to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ pump / N-K-edge NEXAFS probe spectroscopies of *trans*- and *cis*-azobenzene.

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Mean-Field Dynamics of Curvilinear Centroids: Tackling the Curvature Problem

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Popular path-integral methods for approximating the quantum dynamics of condensed-matter systems all encounter problems when simulating infra-red absorption spectra. In particular, ring-polymer molecular dynamics (RPMD) exhibits spurious resonances with the internal ring-polymer modes [1,2], and its thermostatted variant TRPMD produces artificially broadened line-shapes when subjected to a white-noise thermostat [3]. The recently proposed coloured-noise TRPMD yields improved predictions in the stretch region, at the expense of the low-frequency part of the spectrum [4]. Centroid molecular dynamics (CMD) suffers from no such artefacts, but runs into the *curvature problem* at sufficiently low temperatures, resulting in artificial red-shifts and line-shape deterioration [2]. We present a new path-integral method that generalises the mean-field centroid dynamics of CMD to *curvilinear* coordinates. A judicious choice of these coordinates allows us to eliminate the curvature problem in our test systems, ranging from two-dimensional models to q-TIP4P/F liquid water and ice [5]. We present the results of our simulations alongside exact quantum predictions when such are available, and approximate wavefunction-based calculations otherwise. We show that the method performs well over a broad range of temperatures and discuss its generalisations to other systems.

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Reduced-scaling correlation methods for the excited states of large molecules

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A framework for the reduced-scaling implementation of excited-state correlation methods is presented [1]. An algorithm is introduced to construct excitation-specific local domains, which include all the important molecular orbitals for the excitation as well as for the electron correlation. The construction of the resulting compact domains can be performed with cubic scaling using the local density fitting approximation [2], and the sizes are further decreased utilizing our reduced-cost techniques developed based on the natural auxiliary function and local natural orbital approaches [3, 4]. Additional methodological improvements for the evaluation of density matrices are also discussed. The results of benchmark calculations performed at the second-order algebraic-diagrammatic construction level are presented, and it is demonstrated that the speedups achieved are significant even for systems of smaller than 100 atoms, while the errors introduced by our approximation are highly acceptable. Our results show that the new reduced-scaling algorithm allows us to carry out correlated excited-state calculations using triple-ζ basis sets with diffuse functions for systems of up to 300 atoms or 10000 atomic orbitals.

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Frequency Domain Density Matrix Renormalization Group Algorithms for Dynamical Correlation Function of Molecular Aggregates at both Zero and Finite Temperature

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Recent work of our group [1] presented the time dependent density matrix renormalization group (TD-DMRG) approach at both zero and finite temperature for vibronic model to calculate the linear spectrum of molecular aggregates. Here we focus on the frequency domain DMRG approaches within the same matrix product states/operators (MPS/MPO) framework: the correction vector approach is extended to finite temperature; the Chebyshev expansion approach is implemented to access the dynamical property of molecular vibronic model. The absorption spectrum of a real molecular aggregate Perylene bisimide at both zero and finite temperature is calculated to show the effectiveness of frequency domain approaches. CV-DMRG and Cheb-DMRG exhibit similar accuracy compared to that of TD-DMRG. Furthermore, CV-DMRG is favorable for pleasingly parallel computation, and Cheb-DMRG could capitalize the fact that the spectral band of vibronic model is much smaller than the full many-body band to greatly reduce the number of expansion terms. The frequency domain treatment provides an efficient and reliable way for the calculation of the dynamical correlation function of molecular aggregates at zero and finite temperature.

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Ultrafast Intersystem Crossing in Third-Row and Fifth-Row Transition Metal Complexes

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Intersystem crossing (ISC) in transition metal complexes is very different from ISC in typical organic molecules. This is due to the electronic structure of these complexes that lead to a high density of excited electronic states as well as very large spin–orbit couplings due to the high nuclear charge of the metal center. Here, we compare the ultrafast ISC mechanism of two prototypical transition metal complexes, the third-row complex $[Fe(CN)_4$(2,2'-bipyridine)$]^{2-}$ and the fifth-row complex $[Re(CO)_3$(imidazole)(phenanthroline)$]^{+}$. Both complexes have been assigned ISC on a 100 fs time scale by ultrafast spectroscopy in aqueous solution.[1, 2] However, considering the nuclear charge of the two metals, the Re complex should exhibit significantly faster ISC than the Fe complex. By extensive simulations using the Surface Hopping including Arbitrary Couplings (SHARC) [3] method, we show that indeed the ISC mechanisms of these two complexes are different. Most prominently, we provide evidence that ISC in the Re complex can be clearly separated into electronic ISC and nuclear-relaxation-driven ISC, whereas in the Fe complex electronic and nuclear effects cannot be separated.

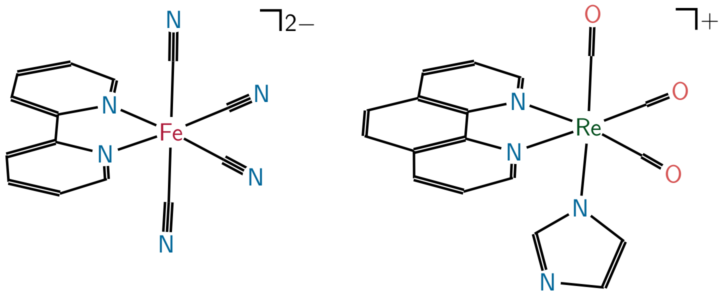

Figure 1: Chemical structures of $[Fe(CN)_4$(2,2'-bipyridine)$]^{2-}$ and $[Re(CO)_3$(imidazole)(phenanthroline)$]^{+}$.

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Constant-Uncertainty Molecular Dynamics. A Practical Method for Approximating Quantum Dynamics?

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Constant-uncertainty molecular dynamics [1] (CUMD) has been proposed as a "simple and efficient" method in which quantum effects can be incorporated into classical molecular dynamics simulations. The method has been shown to give better agreement with exact quantum mechanical results compared to ring-polymer molecular dynamics [2] (RPMD) for one-dimensional test systems. The method uses RPMD to set up an ensemble of classical particles and then evolves them subject to a constraint between the positions and momenta of the particles (based on the uncertainty principle). We find that the constraint cannot be integrated as it contains terms which are non-linear with respect to momenta; this results in the method using an ad-hoc fix, causing it to be inefficient and algorithmically unstable. As a result, it is unlikely that CUMD can be extended to larger, more realistic systems. However, we use the first step in the method (momenta rescaling of the RPMD beads) as a method in its own right and test it on further 1D and 2D systems.

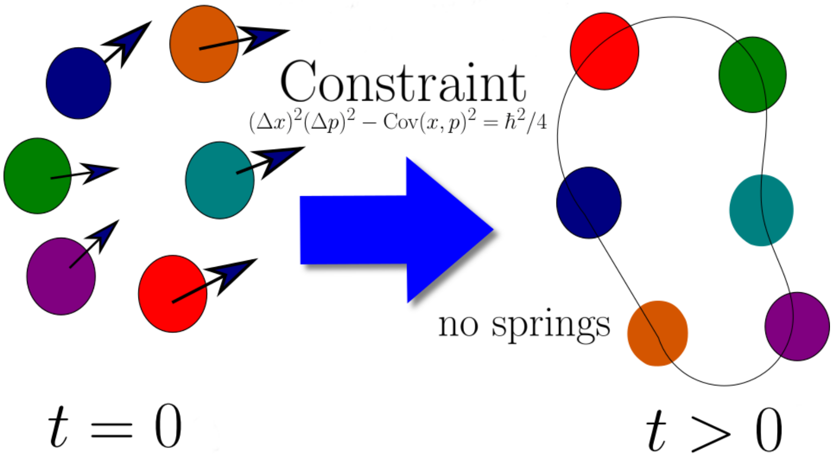

Figure 1: *Idea behind constant-uncertainty molecular dynamcis.*

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Poster: P2-61

A comparative study of CdH and N_2 systems in their ground electronic states between Hylleraas, Varandas and Aguado-Paniagua potentials

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Egil Andersen Hylleraas (1898-1965) made numerous contributions to the development of Atomic and Molecular Physics [1]. In 1935, Hylleraas [2] focused his interests on potential energy curves (PECs) of diatomic species. He proposed a potential containing six fitting parameters [3]:

$$\begin{aligned} V_{HY} = F + -D - D\xi^2, \quad 1 - \xi = \frac{(1+a)(1+c)(x+b)}{(1+b)(x+a)(x+c)}, \\ x = e^{(1+k)\rho}, \quad \frac{1}{1+k} = \frac{1}{1+a} + \frac{1}{1+c} + \frac{1}{1+b}, \\ \rho = \frac{\hbar\omega_e}{2\sqrt{B_e D}} \frac{(R - R_e)}{R_e} \end{aligned} \tag{1}$$

where D, B_e and $\hbar\omega_e$ are spectroscopic constants and R_e is the equilibrium distance. In this work, the evolution in the field of PECs is evaluated, comparing current methods with those proposed more than 80 years ago. For such, we have chosen analytic representations by Hylleraas [4], Varandas [5] and Aguado-Paniagua [6]. For comparisons, the diatomic systems CdH and N_2 both in their respective ground electronic states were selected. These species are the same systems previously used by Hylleraas to test his function [4]. *Ab initio* electronic energies calculated at multireference configuration interaction (MRCI) using AVXZ (X = Q,5,6) basis [7] set were fitted to the mentioned functions. For all studied cases, rovibrational levels, as well as spectroscopic constants, are calculated and compared with available literature data.

Acknowledgments: JPA thanks IF Sudeste MG for the leave of absence during her PhD studies. Financial support from UFJF, CAPES -code 001- are also acknowledged.

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Nonadiabatic Relativistic and QED Correction to the Dissociation Energy of the Hydrogen Molecule Isotopologues

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Theoretical studies of hydrogen molecule is the cornerstone of ultraprecise quantum chemistry. Due to its simplicity, the achieved precision is the highest among all molecules and still has a potential of significant enhancement. Moreover, there are many narrow transitions between rotational and vibrational levels in hydrogen molecules which can, in principle, be measured very accurately what opens new perspectives for determination of fundamental physical constants from its spectra. We search for discrepancies between highly accurate spectroscopic measurements [1,2,3,4] and theoretical predictions based on QED, in order to discover new effects or even new interactions which might result in the developement of the Standard Model. We will present the latest advances in calculation reaching the subMHz level for the dissociation energy of molecular hydrogen isotopoloques. [5,6,7]

The work was supported by the National Science Center (Poland) Grant No. 2016/23/B/ST4/01821

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Scaffold-Based Molecular Design Using a Graph Generative Model

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The vast expanse of chemical space and accumulation of data have been more and more stirring the utilization of machine learning in molecular design. Going beyond allowing fast screening of molecules through efficient prediction of properties, recent advances in generative models enable one to design molecules with desired properties *de novo*. The structural characteristics of generated molecules vary depending on various factors, such as the molecules used for learning and the desired properties. On the other hand, certain applications, particularly in drug design, commonly require new molecules to possess a particular scaffold showing promising functionality. One way of generating molecules having a desired scaffold is defining a generative model whose underlying distribution over molecules is conditioned on the kinds of contained scaffolds. In such a case, however, the probabilistic nature also allows molecules with irrelevant scaffolds, and there can be limitations in categorically representing arbitrary kinds of scaffolds. To tackle these problems, we developed a scaffold-based graph generative model, realizing the architecture as a variational autoencoder [1]. Our model represents a molecular scaffold as a graph and extends it to a supergraph by sequentially adding vertices and edges. By learning the strategy of adding atoms and bonds to scaffolds, our model guarantees with certainty the existence of a desired scaffold in the generated molecules and is free from the representability of scaffold kinds. Our evaluation using unobserved as well as observed scaffolds shows that nearly all of the generated graphs conform to valid valency and that nearly all of the resulting molecules are distinct. When singly or jointly conditioned on molecular properties such as the molecular mass, topological polar surface area, and octanol–water partition coefficient, our model showed good control over the properties in that the property values of the generated molecules had mostly tolerable deviations from the target values. Upon these results, we hope our present work provides a promising approach to designing novel molecules with retained core structures and controlled properties.

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Insights into basis-set convergence from diagrammatic decomposition

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We investigate the basis-set convergence of coupled cluster singles and doubles correlation energies. An analysis of different diagrammatic contributions in the amplitude equation shows that the second-order energy together with the particle-particle ladder term play a significant role for the energy convergence. Our findings are used to formulate an efficient basis-set extrapolation scheme that is applied to atoms, molecules, and solid-state systems.

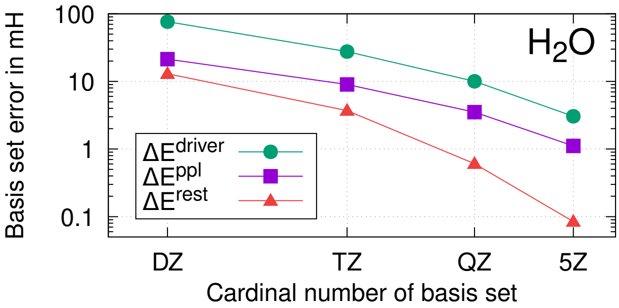

Figure 1: *Absolute basis set error of CCSD valence electron correlation energy contributions for* H_2O *using the aug-cc-PVXZ basis sets. The second-order energy* ($\Delta E^{\mathrm{driver}}$) *and the particle-particle ladder contribution* (ΔE^{ppl}) *show a different convergence compared to all other contributions* (ΔE^{rest})*. The reference energy is approximated using the aug-cc-PV6Z basis set.*

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New insights into the ground and excited states properties of ThO and ThS from 4-component theories

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We present a comprehensive relativistic coupled cluster study of the electronic structures of the ThO and ThS molecules in the spinor basis. Specifically, we use the single-reference coupled cluster and the multi-reference Fock Space Coupled Cluster (FSCC) methods to model their ground and electronically-excited states [1]. Two variants of the FSCC method have been investigated: (a) one where the electronic spectrum is obtained from sector (1,1) of the Fock space, and (b) another where the excited states come from the doubly attached electronic states to the doubly charged systems (ThO^{2+} and ThS^{2+}), that is, from sector (0,2) of the Fock space. Our study provides a reliable set of spectroscopic parameters such as bond lengths, excitation energies, and vibrational frequencies, as well as a detailed analysis of the electron correlation effects in the ThO and ThS molecules [2].

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Is it possible to predict excess properties of mixed solvents by *ab initio* molecular simulation?: Effective fragment potential version 2 – Molecular dynamics (EFP2-MD) Simulation study

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Effective fragment potential version 2 - molecular dynamics (EFP2-MD) simulations, where the EFP2 is a polarizable force field based on ab initio electronic structure calculations were applied to water-methanol binary mixture. Comparing EFP2s defined with (aug-)cc-pVXZ (X = D,T) basis sets, it was found that large sets are necessary to generate sufficiently accurate EFP2 for predicting mixture properties. It was shown that EFP2-MD could predict the excess molar volume. Since the computational cost of EFP2-MD are far less than ab initio MD, the results presented herein demonstrate that EFP2-MD is promising for predicting physicochemical properties of novel mixed solvents.

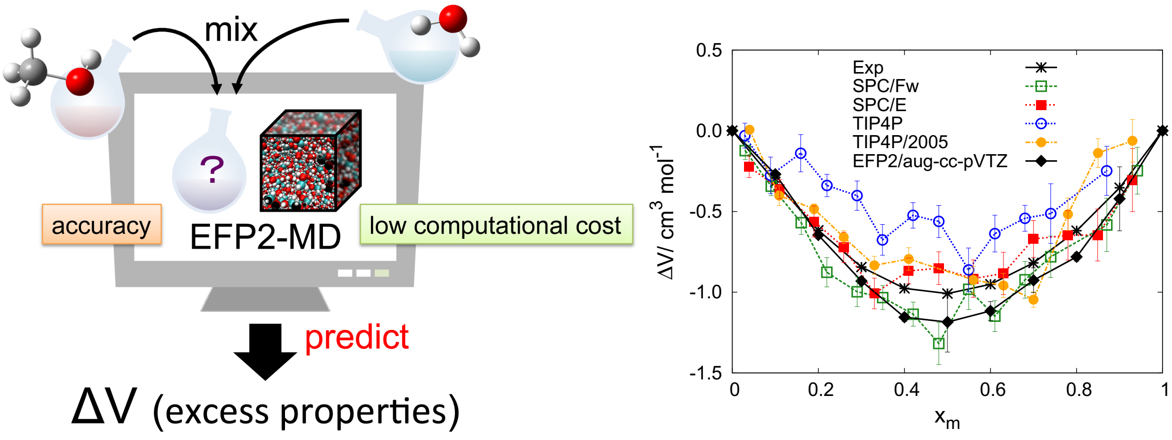

Figure 1: Excess molar volume (ΔV) of a water-methanol mixture at ambient conditions (1 atm, 300 K) simulated by EFP2/aug-cc-pVTZ-MD. For references, experimental and classical MD simulation results are also shown.

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The Peculiar Case of Oxo-Mn(Salen)

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The oxo-Mn(Salen) molecule has been a subject of numerous computational studies motivated by its role in catalysis of the enantioselective epoxidation of unfunctional olefins. Its closely lying singlet and triplet states pose a considerable challenge due to its multireference character, which is the reason why the system has been used repeatedly to assess the performance of methods designed for treatment of strongly correlated systems. One of the frequently applied methods is density matrix renormalization group (DMRG), especially combined with the CASSCF approach [1-4]. More recently, even the effects of dynamic correlation has been examined [3,4], however, the underlying problem remains – the varying reports of different ground states at the DMRG-CASSCF level for calculations performed using active spaces of similar size and in the identical basis sets.

Our aim was to contribute to these efforts by exploring the impact the active space composition and basis set has on the character of the ground state. For this purpose, we selected two active spaces consisting of 22 and 27 orbitals for DMRG-CASSCF calculations. Afterwards, we studied the effect of dynamic correlation using our implementation of the DMRG-based tailored coupled clusters (DMRG-TCCSD) method [4], which newly employs the local pair natural orbital approach (LPNO). With the LPNO implementation we were able to investigate the effect of dynamic correlation up to the quadruple-ζ basis set, which amounts to 1178 basis functions.

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Modeling multistage ultrafast photoinduced electron transfer in complex environments with multiple relaxation timescales

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Photoinduced separation of charges in certain kinds of molecular devices proceeds as a sequence of electron transfer (ET) steps involving several redox centers in the molecule. Since many of these elementary ET reactions are ultrafast, their kinetics and yields are strongly influenced by nonequilibrium dielectric polarization produced in vicinity of the redox sites by optical and radiationless electronic transitions [1]. This feature allows one to control the overall charge separation (CS) yield by adjusting the structure and spatial geometry of the molecule, as well as energetic characteristics of the individual ET steps [2].

The problem of theoretical description of multistage sequential ET was considered recently in the paper [1]. The commonly applied approach here suggests the use of the so-called "energy-gap reaction coordinates", introduced by mapping the environmental degrees of freedom to the vertical energy gaps between the reactant and product states for all elementary ETs. These coordinates however are inappropriate for ultrafast sequential processes, because they are not orthogonal and, therefore, different stages can affect each other's kinetics in the nonequilibrium reactions. A new model of multistage photoinduced ET, proposed in [1], involves the configuration space of *independent* polarization coordinates, and is shown to describe properly the nonequilibrium polarization around the redox sites in the compound. The dimensionality of the space is related to the number of active sites.

We report here an extension of our previous theory [1] allowing one to take into account complex dynamics of dielectric relaxation in vicinity of the redox sites. This extension is important for studying ultrafast multistage ET in non-Debye solvents or biological environments such as polymer blend. Our approach suggests the use of the two coordinate subspaces: the subspace of independent "polarization" coordinates (as mentioned above), and the subspace of "relaxation" modes (as internal coordinates). The new configuration space is formed as the direct product of these two subspaces. The metric properties of this combined space are studied and allow establishing relations between reorganization energies for each elementary ETs, relaxation characteristics of the environment and arrangement of the free energy surfaces (FESs) in the combined space. A general procedure is developed for constructing the diabatic FESs, based on the step-by-step inclusion of electronic states to the model.

Feasibility of the suggested approach is illustrated by its application to a simple model ET reaction involving the molecular compound with 3 redox sites (D, A_1 and A_2) and polar solvent with 2 relaxation times (τ_1 and τ_2). The resulting mathematical model is shown to be fully consistent with the specific models of Najbar/Tachiya (2-stage ET) and Sumi/Marcus (ET in 2-mode environment) developed earlier [3,4].

This work was supported by the Russian Science Foundation (project #16-13-10122).

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An experimental and Molecular Approach of the Anticancer Action of RGD-Peptide Lunasin

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Lunasin is a cancer-preventive peptide isolated from soybean, wheat, barley and other seeds. This compound contains 43 amino acid residues with a cell adhesion motif constituted by arginine-glycine-aspartic acid (RGD) and a carboxylic acid tail of nine aspartic (D) acids [1]. The conformational profile of lunasin has been theoretically studied by means of molecular dynamics [2]. Here, our main objective was to get insights about adhesion of lunasin to cancer cells. Both experimental and computational analyses were carried out to study chemical and physical interactions between lunasin and integrins. Different cancer cell (gastric, colon, and hepatocarcinoma) lines were used to evaluate the lunasin's capacity to adhere cells. First results demonstrated that this ability was dependent on the cell line that could be due to the different level of integrin expression. Computational analysis was carried out with lunasin (model) and other RGD-peptides. Once RGD sequence serves as the primary integrin recognition, its structure and electronic properties has have been studied (Figure1). The calculations were performed at $\mathrm{CAM-B3LYP/6-31+G(d,p)}$ level of theory in the gas phase and in solution using GAUSSIAN09 program [3]. Besides, theoretical models of RGD-water-aspartic acid are being proposed. The next step is to obtain structural and energetic data that allow understanding the lunasin-integrin interactions. Changes of properties like temperature, pressure, concentration and solvent during the process are being evaluated.

The authors would like to acknowledge UFJF by the visiting professor program and CAPES, CNPQ and FAPEMIG for financial support. We also thank the NEQC-UFJF and the LCAD-UNILA for the computational facilities.

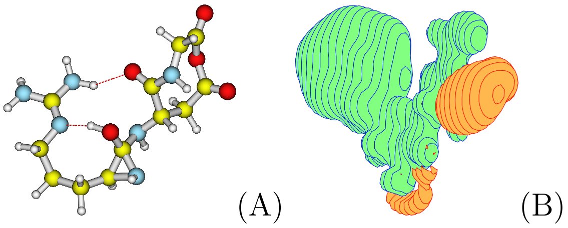

Figure 1: RGD sequence. (A) Optimized geometry and (B) electrostatic potential energy map at $\mathrm{CAM-B3LYP/6-31+G(d,p)}$.

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Local hybrid exchange-correlation functionals based on the static dielectric function

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Kohn-Sham density functional theory (KS-DFT) provides an appealing cost/performance ratio, but its accuracy crucially depends on the choice of the (approximate) exchange-correlation (xc) functional. A new class of flexible, accurate, and efficient functionals - local hybrid functionals (local hybrids) – emerged during the past 16 years [1]. Local hybrids replace the constant exact-exchange (EXX) admixture of traditional (global) hybrids by a real-space-dependent one, governed by a so-called local mixing function (LMF). The latter is a key ingredient in constructing local hybrids, and a variety of different LMFs are known [1].

In this work we construct the LMF as an inverse of the static dielectric function, ε_s^{-1} ("d-LMF"), following the concept of screened Coulomb interactions of electrons in semiconductors [2-4]. We build ε_s as a parameterized function of the local ionization potential (LIP), defined in refs. [5,6]. Our ansatz for the LIP is more flexible than the original one ($\frac{1}{8}\left|\frac{\nabla\rho}{\rho}\right|^2$, where ρ is the electron density) and employs, in addition to the gradient of the density, also its Laplacian. The theoretical foundation of such d-LMFs is solidly grounded in the idea of screening exact exchange locally and they thus provide a more satisfactory justification than some other proposals in the literature, while being sufficiently flexible to suggest practical usefulness. They furthermore justify the use of the reduced density gradient in some previously suggested LMFs. Other crucial ingredients of local hybrids are the semi-local exchange-energy density (which is mixed with the EXX one) and the semi-local correlation energy. PBE exchange [7] and B95 correlation [8] turned out to be a particularly successful combination in conjunction with the d-LMF. Our preliminary validation studies of the resulting local hybrids are promising: the functionals yield good results simultaneously for atomization energies, reaction barriers, total atomic energies, and some other properties. In this work we also analyze d-LMFs in the context of known exact constraints.

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MRChem, a quantum chemistry code with unlimited basis sets. Parallelization and scaling

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MRChem completely avoids the use of traditional Gaussian type basis sets. Instead the real space is subdivided into smaller regions according to the shape of the functions, based on multiresolution analysis. The division of space is done dynamically, to guarantee a predefined precision, without predefined limited basis set. For small systems with low accuracy, this is not a very efficient approach. But for larger systems or if high accuracy is required, the method is expected to be competitive with other methods. In our present implementation, systems with hundreds of electrons can be described. The problems of truncations and near linear-dependencies of the basis set are avoided naturally. The intrinsic adaptation of the grid to the actual functions, leads directly to a decrease of computation time for long range interactions. We present the parallelization strategy adopted, and examples of scalability for large molecules.

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Full Wave Function Optimization of Transition Metal Compounds with Quantum Monte Carlo

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An accurate characterization of the bond cleavage between transition metals and main group elements is of crucial importance in order to elucidate catalytic processes. These systems often exhibit large non-dynamic correlation which still poses a great challenge for high-level theoretical methods. The quantum Monte Carlo (QMC) approach offers an elegant way to tackle the problem of unfavorable scaling with respect to the number of electrons and CPUs, that traditional wave function methods usually suffer from, due to its highly parallel regime.

The wave function ansatz that we employed in this study corresponds to a linear combination of configuration state functions (CSFs), multiplied by a totally symmetric Jastrow correlation factor. We partially and fully optimized the Jastrow, orbital, and CI parameters of complete active space wave functions with respect to the energy within the variational Monte Carlo (VMC) framework. Effective core potentials (ECPs) are used for all calculations. We present accurate dissociation energies for different transition metal compounds at multi-reference diffusion Monte Carlo (MR-DMC) level. The key role can thereby be ascribed to the optimization of the molecular orbitals in the presence of a Jastrow correlation factor. We additionally show that the fixed-node error in diffusion Monte Carlo (DMC) can be systematically reduced by optimizing the multi-configuration guide functions. Our approach is able to yield an accurate description of transition metal compounds with wave functions generated from a small, physically motivated active space.

Poster: P2-73

Relativistic coupled clusters externally corrected by four-component DMRG

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There are three essential problems in computational relativistic chemistry: electrons moving at relativistic speeds, degenerate energy levels and dynamical correlation. Currently available quantum-chemical methods are capable of solving systems with one or two of these issues. However, there is a significant class of molecules, in which all the three effects are present. These are the heavier transition metal compounds, lanthanides and actinides with open d or f shells. For such systems, sufficiently precise numerical methods are not available. In this project, we propose to combine two numerical methods in order to address this challenging class of molecules. These are the relativistic versions of coupled clusters method and density matrix renormalization group (DMRG) method. According to our best knowledge, this is the first relativistic implementation of the coupled cluster method externally corrected by DMRG.

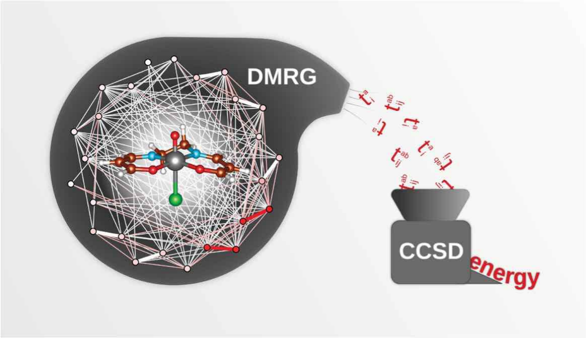

Figure 1: Graphical scheme of coupled clusters externally corrected by DMRG [2].

In the externally corrected approach, first a DMRG calculation is done on the most important part of the active space, keeping the rest of the system fixed. This accounts for the static correlation. Then a CC calculation is performed on the rest of the system, keeping in turn the DMRG part fixed. This captures the dynamical correlation. In other words, the DMRG calculation accounts for the multireference nature of the system, and the following CC calculation includes the effects of dynamical correlation. Already the simplest version thereof, the tailored CCSD (CC with single and double excitations) approach [1], yields very promising results [2]. Remarkably, all previous approaches based on the use of DMRG output in another method have so far been non-relativistic, leaving the relativistic domain unexplored - until now

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Free energy of adsorption evaluation at the metal/liquid interface

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Metal/liquid interfaces stand out by their increasing importance in catalysis and their computational complexity. One of the biggest challenge of this domain is to be able to evaluate the adsorption free energy of a given compound at a metal/liquid interface. Two key ingredients are necessary to reach this goal. The first is a methodology to tackle the problem of the sampling of the water dynamics at the interface while dealing with the costly simulation of the metallic phase. We propose, herein, a computational package that is a refined implementation of the scheme proposed by Steinmann *et al.*[1]. It can be used to compute the adsorption free energy of any molecule at a metal/liquid interface. But this methodology also implies the need of a classical force-field that can accurately describe metal/liquid interactions. This force-field is therefore the second key element needed to address this challenge. Here, we propose the use of a previously published force-field: GAL17 [2] as a first description of the interaction, but also a new currently developed force-field to improve its performances and applicability.

The computation package relies on both quantum and classical calculation, currently performed in VASP and AMBER, respectively. Indeed, the free energy difference is separated in two terms. The first can be evaluated *in vacuo*, at a DFT level and consists in a simple adsorption energy of the molecule on the free metallic surface. The second accounts for the reorganization of the solvent structure that is due to this adsorption and is computed thanks to the Thermodynamic integration method. It relies a sufficient sampling of the reorganization of the water phase, induced by the adsorption of the molecule. Once combined, these two terms provide the desired complete adsorption free energy from the bulk liquid to the water/metal interface.

The chosen force-field is, therefore, the GAL17 force-field that has shown some promising results on Pt (111)/water interfaces. But in this work, we also introduce a novel description based on locally defined metallic surfaces. The extended force-field has been parametrized for 10 noble metal surfaces, i.e., the 100 and 111 facets of Cu, Ag, Au, Pd and Pt. The structuration of the interface obtained with this force field is illustrated in comparison to the METAL force-field which only relies on Lennard-Jones parameters for the interaction between water and metal surfaces.[3]

The combination of this method and force-field could therefore finally achieve the difficult task to provide a physically sound and easy-to-use tool to evaluate any kind a adsorption free energy. Thus, it could be of a tremendous help in the development of numerous catalyst and materials.

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Efficient geometric integrators for nonadiabatic quantum dynamics. II. The diabatic representation

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The first- and second-order split-operator algorithms are widely used integrators for solving the time-dependent Schrdinger equation. These two integrators preserve some important geometric properties of the exact evolution operator: both are unitary and symplectic while only the second-order split-operator algorithm is time-reversible [1]. Higher-order split-operator based integrators are not commonly used because they are thought to be inefficient due to the large number of Fourier transforms they require. The aim of this study [2] is to show that higher-order integrators based on the split-operator algorithm can be much more efficient (by orders of magnitude) if higher accuracy is desired.

For this, the first- and second-order split-operator algorithms were implemented. In addition, we also implemented several higher-order integrators by composing the second-order split-operator algorithm with different composition schemes [3-6]. To test the different integrators, we performed a convergence analysis by computing the photodissociation of NaI on a two-state one-dimensional [7]. The effect of dimensionality on the efficiency and accuracy of the integrators was also explored using a three-state three-dimensional model of pyrazine [8].

From the results, we observe that the higher-order integrators converge faster, in the time step, and are also more efficient than the first- and second-order integrators in both one- and multi-dimensional systems. We also confirm that, as long they are obtained using symmetric composition methods, the higher-order integrators preserve all the geometric properties of the second-order split-operator algorithm.

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A computational protocol for calculation of IR and Raman spectra for solvated systems

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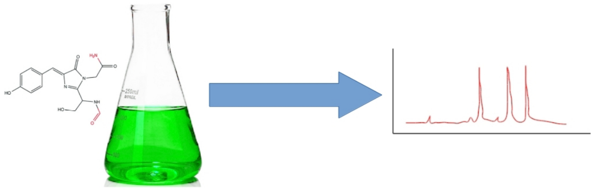
The combination of focused polarizable embedding methods[1] with purely analytical solutions of quasi-energy derivatives[2] is a powerful tool for accurately calculating spectroscopic properties of molecules embedded in large and complex molecular environments. It thus opens a path for determining a wide range of properties for both biomolecules and general solutions. We here present a protocol for how to determine IR and Raman spectra for molecules in solution, with main emphasis on the quantum chemistry program LSDalton[3, 4] and software libraries FraME[5], which handles the polarizable embedding part, and OpenRSP[6, 7], which determines the analytical quasi-energy derivatives.



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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 real systems.

Free energy reaction profile of the desuccinylaiton catalyzed by Sirtuin 5

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Human sirtuin 5 is an NAD$^+$ dependent desuccinylase [1,2]. Deregulation of this activity is connected to several human disorders, therefore, it is important to gain in depth knowledge of its reactivity [2]. One major problem is that most techniques to characterize enzymatic reactions, especially non-dynamic schemes, strongly depended on the chosen educt conformation. A start-frame, necessary for all approaches, is usually chosen from an MM-MD simulation. Since not all educt conformations are reactive, one has to identify suitable periods within the MM-MD simulation to obtain a realistic estimate of a reaction mechanism, before applying cost intensive QM/MM methods [3]. Thus, we utilized machine learning to distinguish suitable start-frames and to discover relevant structural features for the initial step of the desuccinlyation. Subsequent umbrella sampling [4] and the weighted histogram analysis method [5,6] were employed to compute the free energy reaction profile. The computational investigation lead to the conclusion that the nicotinamide cleavage, the first step of the desuccinylation, shows a SN2 type reaction mechanism.

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Insights into S_2 population trapping of uracil using trajectory surface hopping dynamics

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The photophysics and photochemistry of DNA/RNA nucleobases have been extensively investigated during the past two decades, both experimentally and theoretically. The ultrafast relaxation of the canonical nucleobases following photoexcitation is of significant interest when it comes to understanding how nature has ensured their photostability. Here we study the excited state dynamics of uracil which is a nucleobase found in RNA. Although theory and experiment have shed a significant light in understanding the photoexcited dynamics of uracil, there are still disagreements in the literature about specific details. The population trapping in the S_1 minimum is universally accepted. However, the trapping in S_2 has been a contentious topic because the height of the barrier on the S_2 state calculated using different electronic structure methods varies widely depending on the method. In order to examine how the dynamics is influenced by the underlying electronic structure theory, we have performed the excited state dynamics of uracil using on-the-fly trajectory surface hopping method on potential energy surfaces calculated at different electronic structure theory levels to investigate the effect of the barrier on the decay dynamics.

NMR parametrs of Hg$\cdots$H$_2$O complex: relativistic four-component calculations.

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Main objective of the project was to calculate dependencies of nuclear shielding constants of ^{199}Hg, ^{17}O and ^{1}H and indirect spin-spin coupling constants on geometric parameters of Hg$\cdots$H$_2$O complex. In case of systems that include a heavy atom, mercury in particular, it is essential to perform all the calculations with a method that takes relativistic effects into account. That is why, NMR parameters studied in this project were computed with relativistic four-component DFT method.

Before calculating NMR parameters we studied potential energy surface of the dimer by means of CCSD(T) and DFT methods. CC theory is one of the most mathematically elegant techniques for estimating electron correlation energy and, thus, it is also one of the most popular methods of computations in cases, where correlation energy plays a key role in obtaining results in agreement with experiment. That is why, the CC results were considered benchmark for further density functional theory (DFT) calculations with the use of a wide variety of exchange-correlation functionals, for example, B3LYP, BLYP and PBE0. Moreover, some interesting results with regard to equilibrum geometry of the system were obtained. DFT calculations gave a global minimum with mecury atom on C_{2v} axis of water molecule, whereas in case of CCSD(T) the complex in eguilibrium dis not have C_{2v} symmetry.

After that NMR parameters were calculated at the DFT level with four-component relativistic Dirac-Coulomb Hamiltonian since there is currently no implementation of four-component coupled-cluster theory for calculating NMR parameters. In addition to this, some of the calculations were also performed with nonrelativistic Hamiltonian or a relativistic Hamiltonian that did not take spin-orbit effects into account. This enabled us to study the importance of relativistic effects, the effects of spin-orbit splitting and also the HALA (heavy-atom-on-light-atom) effect. It turned out that mercury atom in the neighbourhood of water molecule has significant impact on the values of the proton and oxygen shieldin constants and on the spin-spin coupling constants between oxygen and hydrogen atoms. All of the calculated shielding constants increase with the increase in the distance between mercury and oxygen atoms. σ_O at assumed equilibrium geometry is about 2 ppm smaller than in single water molecule and σ_{Hg} at equilibrium geometry is 12 ppm smaller than in single mercury atom.

The influence of the metal-ligand charge transfer effects on the structural stability and the strength of the spin-orbit coupling in Ni(II)-based metal-ligand complexes

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The structural stability, charge transfer effects and the strength of the spin-orbit couplings in different Ni(II)-ligand complexes with square-pyramidal and octahedral coordination have been studied at M06/def2-TZVP level of theory. Accordingly, two different, porphyrin- and diketo-pyrphyrin-based four-coordination macrocycles as planar ligands as well as pyridine, pyrrole and mesylate anion molecular groups as vertical ligands were considered in order to build the square-pyramidal and octahedral coordination configurations. For each molecular system the identification of equilibrium geometries and the intersystem crossing (the minimum energy crossing point) between the potential energy surfaces of the singlet and triplet spin states is followed by computing the spin-orbit couplings between the two spin states. Structures, based on the diketo-pyrphyrin macrocycle as planar ligand, show stronger five- and six-coordination organometallic complexes due to the extra electrostatic interaction between the positively charged central metal cation and the negatively charged vertical ligands (See at Figure 1 the electrostatic potential map of the two macrocycles). The results also show that the magnitude of the spin-orbit coupling is strongly influenced by the atomic positions of deprotonations of the ligands and implicitly the direction of the charge transfer between the ligand and the central metal ion.

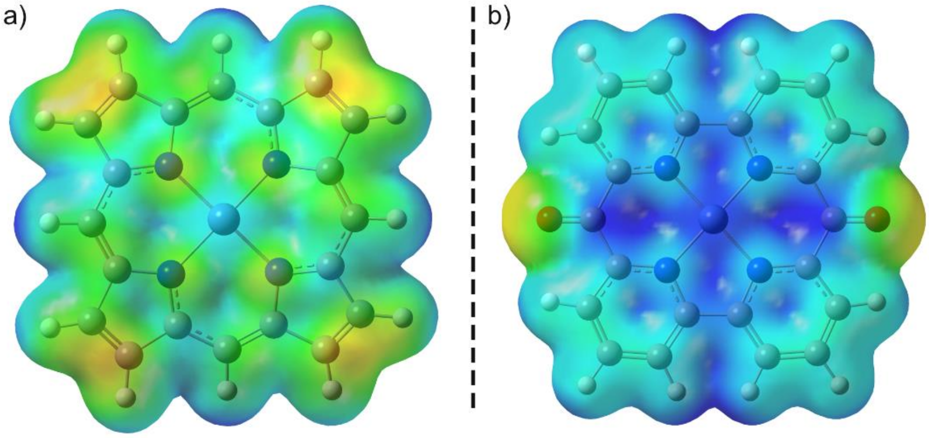

Figure 1. The two maps of the electrostatic potential (e_{min}=0.1*e* and e_{max}=0.3*e*) for the Ni(II)$^{2+}$–porphyrin^{2-} (*a*) and of Ni(II)$^{2+}$–diketo-pyrphyrin (*b*) complexes.

Inter- and Intramolecular Hydrogen Bond Strengths Modeled with Quantum Chemistry

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I present the computation of both inter- and intramolecular hydrogen bond strengths from first principles. Quantum chemical calculations conducted at the dispersion-corrected density functional theory level[1] including free energy and solvation contributions are conducted for (i) one-to-one hydrogen-bonded complexes of alcohols to N-methyl pyrrolidinone measured by an infrared spectroscopy method[2] and (ii) a set of experimental intramolecular hydrogen bond-forming phenol and pyrrole compounds,[3] with intramolecular hydrogen bond strengths derived from a nuclear magnetic resonance method. The computed complexation free energies in solution show a good correlation to experiment of $R^2 = 0.69$ with a root mean square error of 4.25 kJ mol^{-1}. The intramolecular hydrogen bonding free energies in solution show an even better correlation at $R^2 = 0.79$ with a root mean square error of 5.51 kJ mol^{-1}. These results can be used as a guide on how to build reliable quantum chemical databases for computed hydrogen bonding strengths.

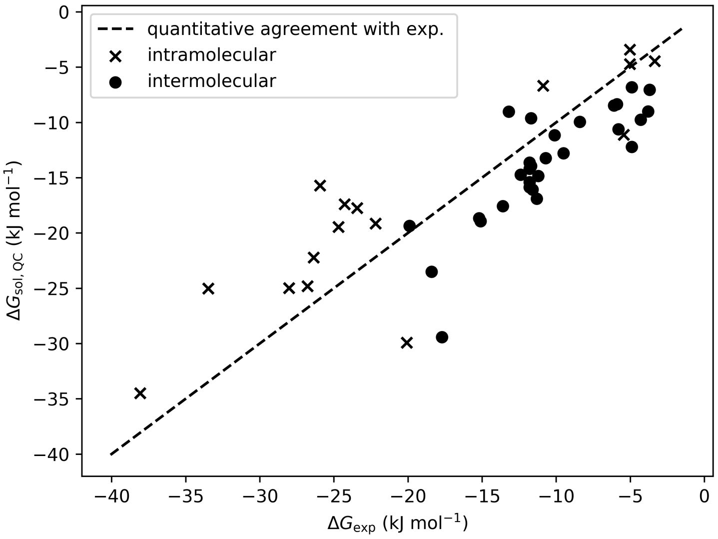

Figure 1: Comparison of experimental and computed free energies in solution for two sets of inter- and intramolecular hydrogen bonds.

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Probing Unusual Hidden Electron Dynamics in Molecules of Biomedical Interest Using Soft PPS Radiation Signatures (RS) in the Framework of Attomechanics Models

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Unbiased RS models were originally introduced to study ultrafast, relatively higher energy events in systems of biomedical interest [1]. That work continued with the study of causal relations between electron attodynamics and the interacting (driving) radiation by measuring characteristic electron RS, that is the observed signatures of such interactions. During the last decade our Polarization Phase Selective (PPS) High Magnetic Field (HMF) instrumentation and methods developed in the framework of new integrative attomechanics modeling significantly improved [2-3]. That allowed inclusion of *soft* HMF PPS RS for studies in the energy region of chemical reactions in large, complex and unstable bio-molecules, "far from equilibrium". Our main challenges are highly selective RS extractions from large sets of interfering components. Scientifically important question we address here is: can these methods probe electrons during protein synthesis and activity, or during interactions with other molecules, like radical SAM. Contrary to what has been suggested in literature, our magnetooptic studies already provide conclusive evidence about electron locations and actions in some studied enzyme reactions. However, some of our most important findings are related to the previously unseen electron dynamics and new protein configurations. Indeed, we can separate signatures from previously indistinguishable proteins that show small structural but paramount activity differences, and we can separate (symmetrical) signatures from recently discovered unusual and previously unseen electron spin-flips [4]. Such events can be hidden or "dark" due to the overlappings and interferences. We estimate that controlling window for such events starts at tens of femtoseconds or in some cases even shorter time.

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* *This work was a part of the UF-PPS Study Project (K. Rupnik PI) which is also performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, and 0654118 and the U.S. Department of Energy.*

Efficient Implementation and Applications of the Doubly Electron-Attached and Doubly Ionized Equation-of-Motion Coupled-Cluster Methods

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The full and active-space doubly electron-attached (DEA) and doubly ionized (DIP) equation-of-motion (EOM) coupled-cluster (CC) methods with up to 4-particle–2-hole (4*p*-2*h*) and 4-hole–2-particle (4*h*-2*p*) excitations, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated ground-state CC wave function of an *N*-electron closed-shell system in order to generate the ground and excited states of the related (*N*±2)-electron species of interest, such as biradicals, have been developed [1,2]. In the case of the DEA approach, the active-space DEA-EOMCC(4*p*-2*h*) method has been augmented by a more cost-effective model at the 3*p*-1*h* level, where both 3*p*-1*h* and 4*p*-2*h* terms are selected using active orbitals [3]. We have recently improved computational efficiency of our original DEA- and DIP-EOMCC codes through 4*p*-2*h* and 4*h*-2*p* excitations [1-3], so that we can now perform routine calculations for sizable molecular problems with ~50–100 electrons and larger basis sets at the highest theory levels including high-order 4*p*-2*h* and 4*h*-2*p* physics. Our plan is to incorporate our new DEA- and DIP-EOMCC routines in GAMESS. By examining the low-lying singlet and triplet states of methylene and trimethylenemethane biradicals, and bond breaking in F_2, we demonstrate that the DEA- and DIP-EOMCC methods with an active-space treatment of 4*p*-2*h* and 4*h*-2*p* excitations reproduce the results of the analogous full calculations at the small fraction of the computer effort, while improving the DEA/DIP-EOMCC theories truncated at 3*p*-1*h*/3*h*-1*p* excitations and making the DEA/DIP-EOMCC results considerably less sensitive to the type of orbitals used in the calculations [1-3]. Using the above and several additional examples, including singlet–triplet gaps in a series of antiaromatic molecules [3,4] and three benzyne isomers [5], we show that our newest variants of the DEA-EOMCC approaches with an active space treatment of 3*p*-1*h* and 4*p*-2*h* excitations and its lower-level counterpart neglecting 4*p*-2*h* contributions are capable of accurately reproducing the results obtained using their relatively expensive parent counterparts with a full treatment of 3*p*-1*h* and full or active-space treatment of 4*p*-2*h* excitations at the small fraction of the computational effort. This work brings us one step closer to a situation, where we may be able to perform routine high-accuracy spin- and symmetry-adapted CC computations for multi-reference (MR) problems, such as those encountered when balancing high-spin and low-spin electronic states, without resorting to genuine MRCC theories.

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Crossover from the quantum to the quasiclassical regime in photodissociation of ultracold molecules

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Chemical reactions and collisions at ultralow energies are dominated by quantum mechanical effects. At higher energies the variety of quasiclassical approaches can be used to understand these processes. The reaction investigated experimentally by the group of Tanya Zelevinsky at the University of Columbia in New York was a light-induced photodissociation of the diatomic strontium molecule. The experiment was performed with the full control over the initial quantum states of the molecule, the final states and the kinetic energy of the fragments.

Quantum model of photodissociation, based on the Fermi golden rule, was successfully applied to explain the photodissociation patterns in the ultracold regime [1]. It was extended to describe the photodissociation in external magnetic field, where the Zeeman coupling of the rotational levels causes the standard selection rules to fail [2].

For high photofragment energies, when dissociation becomes much faster than rotation of the molecule, the widely used quasiclassical model [3] was supposed to correctly describe the process. However, we proved that when the photofragments are identical particles, their bosonic or fermionic quantum statistics can cause this model to fail even for high energies. We propose a corrected quasiclassical model which takes into account quantum statistics [4, 5]. It is confirmed by the experimental results of the Zelevinsky group.

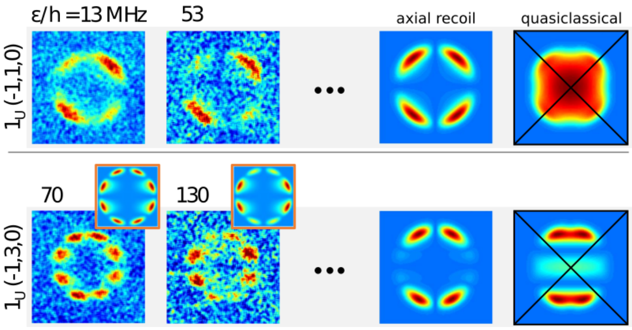

Figure 1: Evolution of photodissociation patterns with energy

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Poster: P2-86

Structure and efficiency in bacterial photosynthetic light harvesting

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Photosynthetic organisms use networks of chromophores to absorb sunlight and deliver the energy to reaction centres, where charge separation triggers a cascade of chemical steps to store the energy. Using a Lindblad master equation approach, we build a detailed model of the photosynthetic antenna complexes in purple bacteria, with a focus on explicitly modelling the interaction with natural, incoherent light and capturing the multiple effects of coupling to vibrational modes with a large range of frequencies. In particular, we include, for the first time, the effect of slow vibrational modes by introducing time-dependent disorder.

We find that the system remains almost entirely in its groundstate for all time, with only a miniscule fraction of excited state present at any given moment. This tiny fraction is, over a time average, in a state very close to the maximally mixed state within each antenna component. Exciton density moves around the antenna with the aid of the vibrational environment, which drives relaxation towards thermal equilibrium, while also continually changing the identity of the thermal state.

Additionally, we apply our model to simple artificial systems with very few structural constraints, demonstrating that efficiency depends more strongly on the proximity rather than the specific spatial arrangements of the chromophores. The high efficiency of these systems offers an explanation for the fact that different organisms achieve extraordinarily efficient energy transport with greatly differing structures. It also paves the way for a new approach to designing artificial light-harvesting devices that are highly efficient and easily synthesised.

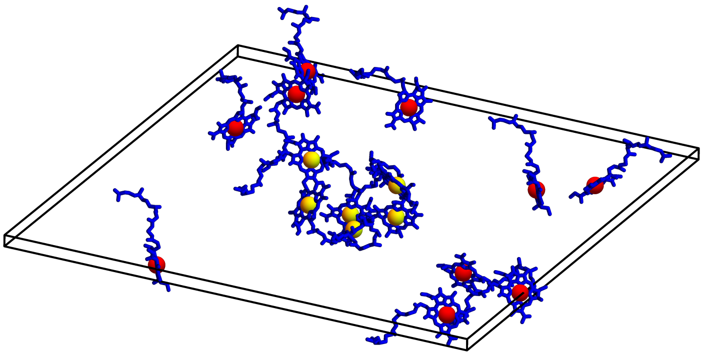

Figure 1: The efficiency of a network of chromophores does not depend strongly on their specific spatial arrangement. We demonstrate this by simulating an artificial network of chromophores placed randomly in a box around a central reaction centre (highlighted with yellow centres).

Spin-mapping approach to nonadiabatic dynamics

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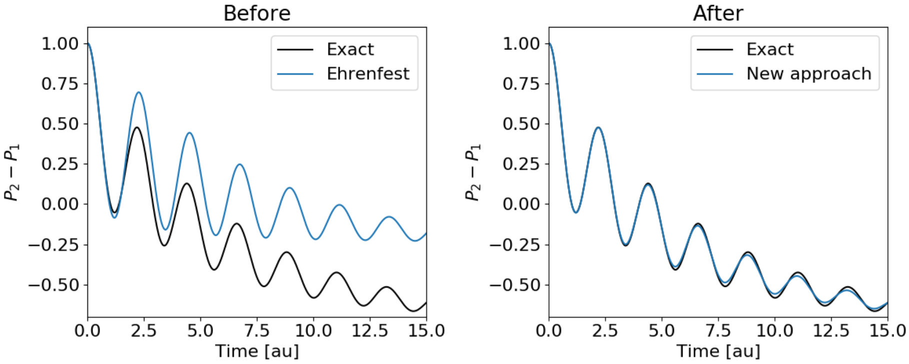
One way to simulate nonadiabatic processes is in terms of classical trajectories on multiple electronic surfaces. A commonly used approach is the Meyer-Miller-Stock-Thoss mapping [1,2] that replaces the electronic levels with a singly excited harmonic oscillator. The mapping is exact on the quantum level, but has some well-known deficiencies when used to generate classical trajectories. Most important is the unphysical flow of electronic zero-point energy between the oscillators. As a consequence, the mapped operators have to be projected back onto the physical subspace of singly-excited oscillators.
We have recently proposed [3] an alternative mapping for two-level systems that requires no such projections. It is based on a coherent-state representation of spin-1/2 systems, which just like the MMST mapping is exact on a quantum level, and gives rise to the same equations of motion. Nonetheless, there are a couple of differences which can be summarized in two main points. First we restrict the distribution of the mapping variables to a sphere of all directions of a fictitious spin vector. Second we construct correlation functions of electronic operators in terms of their Stratonovich-Weyl transforms, which can be interpreted as using the quantum-mechanical magnitude of the spin in place of the classical magnitude.
Our mapping does not add any computational complexity and is as easy to implement as standard MMST-approaches. When comparing to benchmark results for population transfer in various spin-boson systems, we find that our approach is consistently more accurate than both MMST and Ehrenfest dynamics, in particular for asymmetric systems.



Population difference between two electronic states for a spin-boson system that is initially in its excited state. Ehrenfest dynamics predicts completely wrong final state populations, whereas our method is in almost perfect agreement with the exact result.

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Poster: P2-88

Flexible toolbox for calculation of relativistic properties with two-component densities

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Relativistic effects typically play an important role for the theoretical description of heavy-elemental compounds and in calculations of properties that depend strongly on the structure of the electronic wave function close to the nuclei, such as NMR shielding constants. For many purposes, however, it is not necessary to perform four-component relativistic calculations, but quasi-relativistic two-component methods often suffice. This applies even in case of so-called purely relativistic effects, as we have shown for molecular enhancements of a hypothetical electric dipole moment of the electron (eEDM).[1]
Nowadays, many programs are capable of two-component calculations. Nonetheless, the majority of two-component programs is restricted to conventional molecular properties, such as NMR-shielding constants or g-tensors. This is often caused by the fact that the calculation of relativistic molecular properties with one- or two-component wave function requires a proper transformation of the operators into the appropriate picture. The implementation of less conventional properties, such as parity violating energy shifts or other intriguing effects, often is done by hand and not available as an out-of-the-box feature. Thus an automated evaluation of custom one-electron properties with efficiently calculated two-component wave functions is of great use.
In this poster a general formulation of relativistic one-electron properties in terms of density functions is presented, which allows for customized definition of operators within a generic two-component property module. An implementation within a two-component zeroth order regular approximation (ZORA) framework for the use with a modified version of the Turbomole program package[2] is outlined. Within this implementation arbitrary relativistic properties can be calculated, ranging from symmetry violating properties which are of importance for different fundamental physics tests, to conventional hyperfine coupling, electric field gradients or NMR shielding tensors.

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A consistent molecular model to predict the behavior of tetravalent actinides from thorium to berkelium.

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The aim of the present study is to investigate and revisit the behavior of tetravalent actinides from thorium to berkelium in aqueous solution by the use of classical mechanics simulations. While spectroscopy provides a good insight into the interatomic distances, the hydration structure, exchange dynamics and coordination numbers remain quite inaccurate [1]. Our objective is to probe the local structure and explore the trends along the early actinide series in the bulk conditions with classical molecular dynamics (MD) simulations: the only modelling approach that allows us to monitor the dynamics of a hydrated actinide by a large number of water molecules in a long time-scale (> 10 ns). However, the reliability of the MD results entirely depends on the quality of the force-field (FF), i.e., the description of the interaction between the solute and the solvent (An/water molecule interaction), and also on the description of the solvent properties. The FF model that we developed accounts, not only for the standard electrostatic and repulsion interactions, but also for polarization and charge-transfer terms, many-body effects, and explicit hydrogen bonds in the water/water interactions.

Pursuing the efforts initiated by Réal et al. to simulate the Th(IV) and Cm(III) in aqueous solution [2, 3, 4], we present here a consistent force-field model adjusted to state-of-the-art *ab initio* calculations, i.e., without using any experimental input, for the early tetravalent actinides series from thorium to berkelium, and the associated results coming from bulk simulations. The average actinide/water distances almost perfectly agree with the reported EXAFS values and our MD simulations predict that all early actinides hold around 9 water molecules in their first hydration sphere. These results represent a first step towards a better description of these elements in solution or at interface.

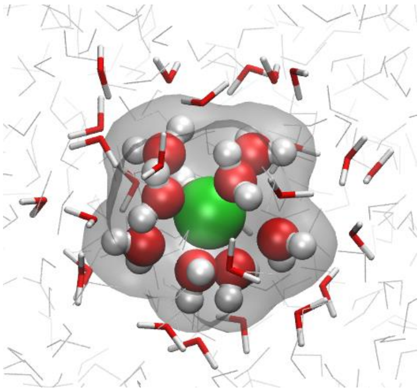

Figure 1: An^{IV} coordination structure by water: an MD snapshot.

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Hybrid QM/MM Dynamics of Complex Systems within the AMOEBA Polarizable Embedding

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In recent years lots of efforts have been devoted in the field of classical molecular dynamics (MD) for the development of force fields that explicitly account for polarization, but still efficient for the study of large systems. They include many-body effects, improving, in principle, flexibility and accuracy. Such improvement is still not enough for the description of many important phenomena in molecular sciences, such as chemical reactivity and photoinduced processes, due to their intrinsic quantum nature. In that respect, Hybrid Quantum Mechanics/Classical methods represents a very promising strategy as They combines the computational efficiency of a classical model with the required quantum description of the subsystem of interest.

In the last years we developed a Born-Oppenheimer (BO) hybrid QM/MM MD strategy, based on the coupling[1, 2] of Density Functional Theory (DFT) and the polarizable AMOEBA[1] force field. This approach involves the interplay between the Gaussian and Tinker suite of programs through a variational formalism allowing for a self-consistent relaxation of both the AMOEBA induced dipoles and the DFT electronic density at each MD step.

In this contribution we will present some new advances in the implementation of the code, and some recent applications involving molecular systems embedded in complex environments, such as DNA or protein matrices.

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Efficient geometric integrators for nonadiabatic quantum dynamics in the adiabatic representation

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Geometric integrators [1] of the Schrödinger equation conserve exactly many invariants of the exact solution. Among these integrators, the split-operator algorithm is explicit and easy to implement but, unfortunately, is restricted to systems whose Hamiltonian is separable into kinetic and potential terms. We present several implicit geometric integrators applicable to both separable and nonseparable Hamiltonians and, in particular, to the nonadiabatic molecular Hamiltonian in the adiabatic representation [2]. These integrators combine the dynamic Fourier method with recursive symmetric composition [3,4] of the trapezoidal rule or implicit midpoint method, which results in an arbitrary order of accuracy in the time step. Moreover, these integrators are exactly unitary, symplectic, symmetric, time-reversible, and stable and, in contrast to the split-operator algorithm, conserve energy exactly, regardless of the accuracy of the solution. The order of convergence and conservation of geometric properties are proven analytically and demonstrated numerically on a two-surface NaI model in the adiabatic representation. Although each step of the higher order integrators is more costly, these algorithms become the most efficient ones if higher accuracy is desired; a thousand-fold speedup compared to the second-order trapezoidal rule (the Crank-Nicolson method) was observed for a wavefunction convergence error of 10^{-10}. In a companion paper [5], we discuss analogous, arbitrary-order compositions of the split-operator algorithm and apply both types of geometric integrators to a higher-dimensional system in the diabatic representation.

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A computational investigation of the effects of solvent-induced electric fields on vibrational frequency shifts

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Computational vibrational spectroscopy serves as an important tool in the interpretation of the experimental infrared spectra. In this work, we benchmarked the computational vibrational spectroscopic methods including normal mode analysis (NMA) and fast Fourier transform dipole autocorrelation function (FT-DAC)[1]. We demonstrated the advantages of the FT-DAC method for flexible and anharmonic systems [1]. Then, we extended the benchmarked DFTB3/FT-DAC model to the condensed phase systems with the combined QM/MM simulations. We have investigated the effects of solvent-induced electric field on vibrational frequency shifts, known as the Vibrational Stark Effect (VSE)[2,3]. We studied acetophenone as the vibrational chromophore in a series of different polar and non-polar solvents and solvent mixtures. Linear correlations between the solvent-induced electric field and the vibrational probes frequency shift were found. An overestimation of hydrogen bonding at the DFTB3 and MM boundary was observed, whereas no such overestimation was showed at the boundary between the DFTB3 and Drude polarisable model. This emphasizes the importance of including explicit polarisations at the QM/MM simulations.

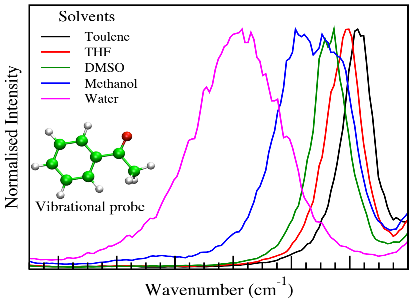

Figure 1: FT-DAC spectra in various solvents

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Poster: P2-93

The Role of Non-Covalent Interactions in the Self-Assembly of Aromatic Peptide Nanotubes

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Self-assembled peptide nanotubes have many potential applications in the fields of energy, nanobiotechnology, and nanomedicine. Peptides serve as excellent building blocks due to their high availability and versatility. Aromatic peptides tend to form dipeptides which then self-assemble into nanotubes. Currently, there is a lack of fundamental understanding as to how these nanotubes assemble. However, it is widely believed that non-covalent interactions between dipeptide units drive this self-assembly. In this study, intermolecular interactions between tryptophan-tyrosine (WY) dipeptides were investigated using various quantum-chemical computational methods. Other analyses such as natural bond orbital and energy decomposition were also applied. Several WY dimer configurations were studied for their structural, energetic, thermodynamic, and spectral properties to gain insight on the non-covalent interactions that take place between WY monomers. Our work confirms the role of π-π stacking, electrostatic, and dispersion forces in the stabilization between WY units, and likely drive aggregation of self-assembled structures from peptide-based molecular frameworks.

The exciting aqueous chemistry of the simplest radical – proton-coupled electron transfer in the reactions of hydrogen atom

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We present our latest theoretical and experimental studies on the reactions of the simplest radical – the hydrogen atom – with a series of halogenated organics in neutral aqueous solutions. The investigated compounds are: monohaloacetates[1] (chloroacetate, bromoacetate, and iodoacetate) and a modified nucleobase, 5-bromouracil. The reactions are studied using density functional theory (M06-2X) in combination with the polarizable continuum model as an implicit description of the water solvent. We also study the effects of the presence of basic buffer anions, such as bicarbonate and hydrogen phosphate, on the reaction mechanisms and rates. The H atoms are generated as primary radicals of the water radiolysis and ionic chromatography is used to measure the yields of halide anions. These systems exhibit a variety of possible reaction mechanisms such as: halogen atom abstractions, H atom additions, H atom abstractions, and the proton-coupled electron transfer (PCET). The latter mechanism is of vast importance to biochemistry, electrochemistry and energy conversion.[2] The possibility of the PCET is especially interesting because, in cases when the proton and electron acceptor sites are spatially distinct, the PCET implies the disintegration of the H atom to the constituting proton and electron thereby representing the most fundamental instance of the process. The addition of the HCO_3^- or HPO_4^{2-} buffer anions, both of which are good proton acceptors, has a potential to accelerate the PCET. The calculations indicate that the PCET, which effectively involves a one-electron reduction of the substrates and hence causes their dehalogenation, is in close competition with the H atom abstraction (chloroacetate) and the direct halogen atom abstraction (bromoacetate). Since most of these processes are dominated by the light particle tunneling, for computing the reaction rate constants we use the variational transition state theory with the semi-classical tunneling corrections in the small curvature regime (SCT).

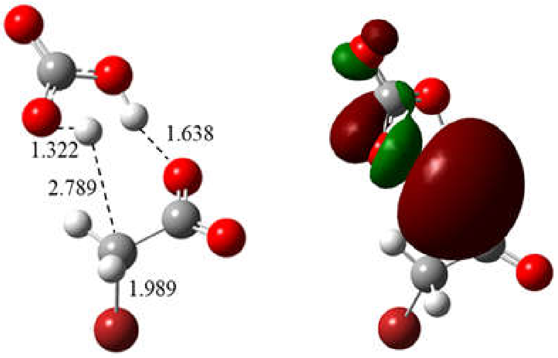

Figure 1: PCET transition state structure and its singly occupied molecular orbital (SOMO) in the reaction of H• with bromoacetate in the presence of bicarbonate (distances in Å).

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Elastic Rate Coefficients of Li + H_2 collisions in the calibration of a Cold Atom Vacuum Sensor

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Ongoing efforts at the National Institute of Standards and Technology in creating a cold-atom vacuum standard device have prompted theoretical investigations of atom-molecule collision processes that characterize its operation [1]. Such a device will operate as a primary standard for the ultrahigh-vacuum and extreme-high-vacuum regimes. This device operates by relating loss of ultracold lithium atoms from a conservative trap by collisions with ambient atoms and molecules to the background density and thus pressure through the ideal gas law. The predominant background constituent in these environments is molecular hydrogen H_2. We have computed the relevant Li+H_2 Born-Oppenheimer potential energy surface (PES), paying special attention to its uncertainty. With increasing accuracy we constructed potentials labeled TZ, QZ, 5Z, and ∞Z, respectively. Coupled-channel calculations are then used to obtain total rate coefficients, which include momentum-changing elastic and inelastic processes. We find that inelastic rotational quenching of H_2 is negligible near room temperature. For a ($T = 300$)-K gas of H_2 and 1.0-μK gas of Li atoms prepared in a single hyperfine state, the total rate coefficients are $6.0(1) \times 10^{-9}$ cm^3/s for both ^{6}Li and ^{7}Li isotopes, where the number in parentheses corresponds to a one-standard-deviation combined statistical and systematic uncertainty. We find that a 10-K increase in the H_2 temperature leads to a 1.9% increase in the rate coefficients for both isotopes. For Li temperatures up to 100 μK, changes are negligible. Finally, a semiclassical Born approximation significantly overestimates the rate coefficients. The difference is at least ten times the uncertainty of the coupled-channel result.

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Nonadiabatic quantum transition-state theory in the golden-rule limit

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In our work, we propose a path-integral method to study non-adiabatic reactions involving two electronic states. Such a reaction cannot be studied using the Born-Oppenheimer approximation. We have recently developed a new quantum transition-state theory to compute reaction rates in multi-dimensional systems in the Fermi's golden-rule regime [1]. Our golden-rule quantum transition-state theory (GR-QTST) is exact in the classical limit for all systems. GR-QTST is related to instanton theory [2], and hence gives excellent estimates of rates in both harmonic and anharmonic model systems even in the deep tunneling regime. Our theory relies on constrained path-integral sampling of dominant energy-conserving paths similar to an instanton. It is applicable to treat chemical reactions in solution, in which the potential energy surfaces exhibit multiple transition states. We show that a related theory known as Wolynes theory [3] can overestimate the reaction rates by multiple orders of magnitude, even for simple one and two-dimensional model systems with two transition states. The rates computed using GR-QTST show excellent agreement with the exact calculations in these systems. Accordingly, our results show that GR-QTST offers a simple approach to accurately calculate electron-transfer rates in complex multi-dimensional molecular systems using a path-integral sampling.

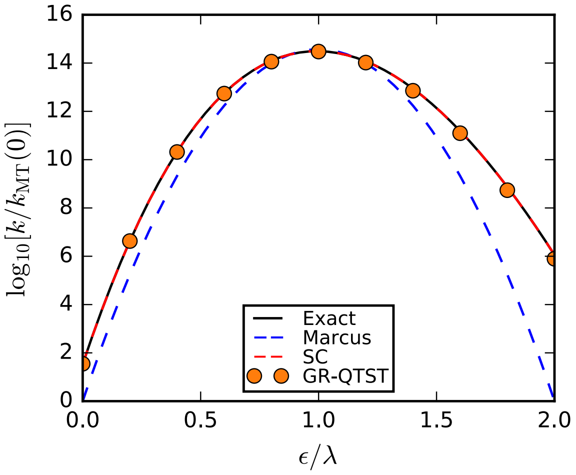

FIG. 1: The plots show the rate constants computed for 8 dimensional system-bath model as a function of bias, ϵ, using various methods. $k_{\mathrm{MT}}(0)$ is the classical Marcus rate at $\epsilon = 0$. 100 ring-polymer beads were used to compute the GR-QTST rates at room temperature. Comparision to rates computed using semi-classical (SC) instanton and exact Fermi's golden-rule methods shows that GR-QTST is very accurate in predicting the electron-transfer rates.

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Periodic MRChem

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MRChem is a numerical real-space code for molecular electronic structure calculations within the self-consistent field (SCF) approximation of quantum chemistry, Hartree–Fock and Density Functional Theory. MRChem uses a multiwavelet (MW) basis, and are used in quantum chemical calculations due to their mathematical properties, such as, error control and low scaling. The code has recently been applied to two large and precise benchmark studies on electronic energies[1] and magnetizabilities and shielding constants[2].

We are currently expanding the code to solve the Kohn–Sham equations for crystalline systems. We give an overview of this work including examples of total energies compared with other solid state codes, and how MWs can be used to systematically increase the accuracy of the result with respect to the basis set.

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Rydberg bonding - the non-valence long-range covalent bond

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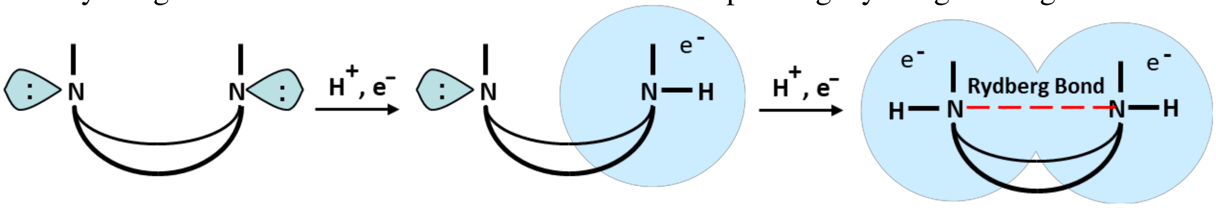
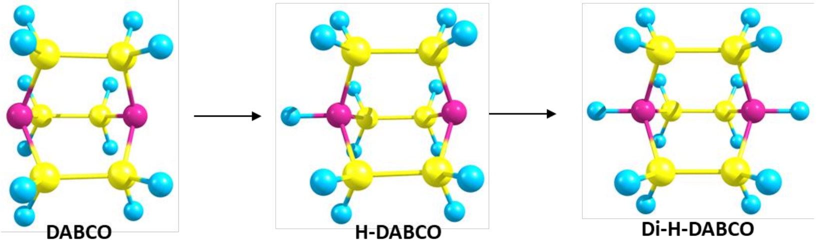
The first experimental study of Rydberg species - •NH4 was reported by Herzberg in 1981 [1]. This radical is not stable, but it could be stabilized by the complexation in ammonia cluster.
3s-AO Rydberg origin was reported for the different alkyl-substituted amines [2,3]. Calculations of pyrrole-ammonia [4], pyrazole-pyrazole and imidazole-imidazole [5] complexes show that the proton shift is escorted by shift of a Rydberg orbital from the excited to the ground state.
Chemical binding of two monovalent Rydberg radicals $\bullet NH_4$ to form a dimer with non-valence Rydberg bond was estimated to be about 8 kcal/mol [6]. However, the dimer $(NH_4)_2$ is unstable towards dissociation into ammonia and molecular hydrogen [7].
The goal of this study is a design of thermodynamically and kinetically stable compounds with two Rydberg radical centers and estimation of the corresponding Rydberg binding:



Different diaza-derivatives of cyclohexane and some polycycles were studied computationally on CASCF, CAS-MP2 and DFT levels of theory. Probably, the optimal position of N-centers for the Rydberg binding is 1,4-diaza location. Addition of hydrogens to the two N-atoms of 1,4-diazapiperazine or DABCO leads to strong and long-range bonding between two Rydberg N-centers. The strength of N-N Rydberg bond could reach 0.9eV as was calculated for the 1,4-dihydro-DABCO adduct (di-H-DABCO). Calculations show both thermodynamic and a kinetic stabilization for the molecules with a Rydberg N-N bond for the different 1,4-diaza-derivatives.



VB analysis of the 3s-3s AOs binding between two N-atoms shows the dominant covalent character of the Rydberg N-N bond.

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Unravelling the Nature and the Timescale of the Dielectric Constant for Organic Semiconductors

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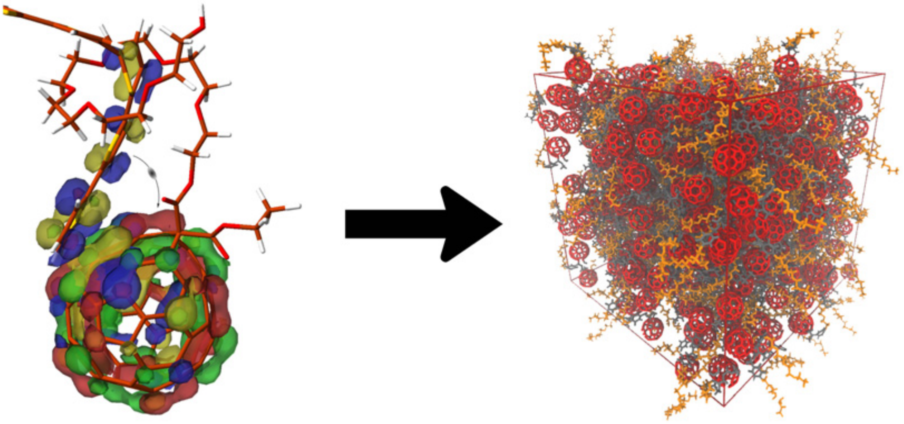
The current generation of organic photovoltaic devices still lacks the required efficiency to be economically competitive. One way to improve this is to use materials with a high dielectric constant, thereby decreasing the effective coulombic attraction between the electrons and holes and therewith facilitating their transport to the respective electrodes without suffering from recombination [1]. A prominent strategy to this end is the use of ethylene glycol side chains, which are known to increase the dielectric constant drastically [2]. However, both the response timescale and a clear molecular understanding of the origin of the contributions are still lacking.

In this poster, we present a multiscale computational scheme to calculate the different contributions (electronic, dipolar and induced) to the dielectric constant. We employ polarizable force fields for molecular dynamics simulations, for which we derive the parameters from quantum chemical calculations. Having access to detailed molecular information, we are able to decompose the dielectric contributions into molecular fragments, which allows us to clearly pinpoint the origin of these contributions. Moreover, our results, for the first time, unravel the timescale of the contributions and shed light on their relevance for high efficiency organic photovoltaics [3].



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Development of the Fragment-Based GW+Bethe-Salpeter Equation Method for Applications to Organic Materials

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Organic electronics based on π-conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the charged-transport levels or optical excitations is essential for understanding the electronic processes governing the device operation and for rationally designing novel materials. The successful theoretical descriptions of charged and neutral excited states requires an accurate quantum mechanical method: in addition, the effects of polarizable environment must be properly taken into account. Here, we present a large-scale GW implementation based on the fragment molecular orbital method [1,2]. The implementation is based on the fragmentation approximation of the polarization function [3] and the combined GW and Coulomb-hole plus screened exchange approximations for self-energies [4]. Our fragment-based method can describe the state-specific polarization effect and the delocalization of charge and excited states on the same footing. The fragment-based GW is demonstrated by applications to an organic semiconductor thin film and a donor/acceptor interface structure. We highlight the impact of the induced polarization effects on the charged and neutral excitations in the organic semiconductors.

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The Role Played by Vitamin A as a Probe in Milk: A Vibrational and Electronic Study

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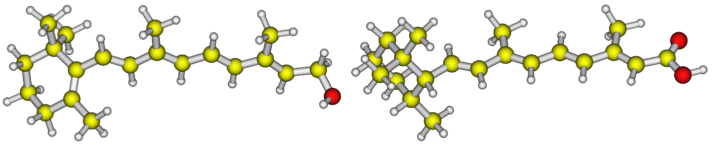
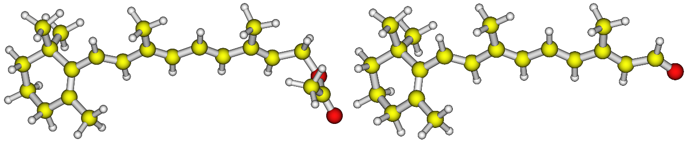
Vitamin A has been employed as a naturally spectroscopic marker in milk. M. Brandão *et al.*, in the frame of time-correlated single photon counting (TCSPC), have observed specific shifts in the electronic spectra and fluorescence of this vitamin from skimmed to milk whole [1]. In this present study it will be investigated which molecular action mechanism can be responsible for such behaviors. For thus, the geometries of retinol, retinyl ester, retinol acetate and retinal were fully optimised at $\mathrm{CAM-B3LYP/6-31+G(d,p)}$ level of theory in the gas phase and in solution. The medium effects were included using the polarizable continuum model (PCM) [2]. The vibrational spectra (Infrared and Raman) were obtained at the same level of theory. Time-Dependent DFT approach [3] is used to study the electronically excited states of retinol, retinyl ester, retinol acetate and retinal. To investigate Time-Resolved Fluorescence measures of retinol in milk, lifetime decays were calculated and compared with the experiment. The obtained results provide theoretical support to the experimental counterparts and rationalisations to changes in average decay lifetime. Our findings contribute to understanding its profile in different environments, either to differentiate types of milk or to assess the quality of dairy products. All calculations were performed using GAUSSIAN09 program [4].

The authors would like to acknowledge Universidade Federal de Juiz de Fora (UFJF) by the visiting professor program and CAPES, CNPQ and FAPEMIG for financial support. We also thank the Núcleo de Estudos em Química Computacional (NEQC-UFJF) and the Laboratório de Computação de Alto Desempenho (LCAD), Universidade Federal da Integração Latino-Americana (UNILA) for the computational facilities.



(a) Retinol (b) Retinyl ester



(c) Retinol acetate (d) Retinal

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Structures of CdSe and CdS nanocluster by ab initio random structure searching

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The properties of colloidal semiconductor quantum dots (QDs) continue to stimulate a lot of interest in a wide variety of field including materials, photonics, energy applications etc. Over the last few years, there has been a lot of interest in ultra-small QDs that do not follow the usual nucleation- and-growth model during the synthesis - so-called Magic-Sized Clusters (MSCs). These MSCs have an advantage of being mono-diapers systems with a number of unusual optical properties including temperature-dependent emission switching [1]. However, despite significant level of interest, the identifying atomic structure of these systems is still a challenge.

We have therefore turned to ab initio structure prediction as a useful tool to aid the analysis of experimental observations and develop an understanding of the structures of the dots. A systematic first principles structure prediction study of $(CdSe)_n$ and $(CdS)_n$ nanoclusters has not been attempted previously, instead guesses are often obtained starting from sections of the bulk crystal that are subsequently relaxed using density-functional theory (DFT). In our research, we have explored the possible space of stable structures of $(CdSe)_n$ and $(CdS)_n$ (n up to 34) more completely using ab initio random structure searching (AIRSS) [2, 3]. Using AIRSS we build libraries and benchmarks for the ground state structures in a more objective way and also provide some reference to predict the nanoclusters structures with AIRSS method. I will present demonstrate how AIRSS allows us to understand the transition from cage to bulk-like structures.

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Quantum-mechanical relations between polarizabilities and geometric properties of atoms

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Many properties of real physical systems can be captured by approaches based on Gaussian wave functions. Among them, the quantum Drude oscillator (QDO) model [1–3] serves as an insightful and efficient approach for the description of atomic response properties as well as van der Waals (vdW) interactions. Within this model, all valence electrons in an atom are represented by a single *Drude particle* characterized by its charge, mass, and characteristic frequency. The Gaussian wave function of the QDO allows to perform analytical derivations of the atomic properties related to vdW interactions, which fulfill several scaling laws valid for real atoms. Particularly, invariants constructed from the dispersion coefficients or the atomic polarizabilities within the QDO model accurately capture real atomic properties [3]. Recently [4–5], this model helped to unveil the non-trivial relation between the dipole polarizability and the atomic volume, $\alpha_{\mathrm{dip}} \propto V^{4/3}$. We have also discovered a very surprising relationship between the multipole polarizabilities and the vdW radius as well as the equilibrium distances in vdW-bonded atomic dimers [6]. Here, we give an overview of all these remarkable findings and show their impact on practical applications. In particular, the parametrization of interatomic vdW potentials becomes now easier due to the obtained quantum-mechanical relations between the polarizability and the equilibrium distances in homonuclear as well as heteronuclear dimers. This reduces the empiricism and improves the accuracy of corresponding approaches. The revealed relations also allow to amend the scheme for evaluating the effective atomic radius in a molecule, which improves the accuracy of computational models for intermolecular interactions like the Tkatchenko-Scheffler method [7].

We acknowledge financial support from the European Research Council (ERC Consolidator Grant "BeStMo"). M. Stöhr acknowledges financial support from the Fonds National de la Recherche, Luxembourg (AFR PhD Grant "CNDTEC").

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Definition of Electrode Potential from Density Functional + Implicit Solvation Theory

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Electrode potential is a general concept, in electrochemistry, which governs the charge transfer reactions such as ion insertion/extraction and reduction-oxidation at electrode/solution interfaces; the electrode potential should be appropriately included in the computational model.[1] In this study, we consider how the standard hydrogen electrode (SHE) potential, which is the equilibrium potential of the charge transfer reaction of H^+/H_2, is theoretically evaluated.

We employed density functional theory (DFT) calculations combined with the effective screening medium (ESM) technique[2] + the reference interaction site method (RISM);[3] ESM-RISM formulation[4] makes it possible to simulate the electrode (+ reactive ions) and the solution based on quantum mechanics and implicit classical solvation model, respectively. Changing the chemical potential of electron, μ_e, referenced to the inner potential Φ_S at the bulk solution region, we compared the grand potentials Ω for the following reaction:

$$H_3O^+ \text{ (1M HCl aq.)} + e^- \text{ (electrode M)} \leftrightarrow 1/2\, H_2 \text{ (gas)} + H_2O \text{ (1M HCl aq.)}$$

In the presentation, we will compare the potential profile of metal/solution/vacuum region obtained from ESM-RISM and the first-principles molecular dynamics calculation using ESM.[5] We further discuss on the difference between μ_e@SHE and the absolute SHE obtained by Trasatti.[6]

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Local or Nonlocal? A Multireference Study of Charge and Exciton Transport in Organic Semiconductors

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Hopping transport of charges or excitons in organic semiconductor layers implies that the hopping quasiparticles (electrons, holes, or excitons) are localized within relatively small regions, such as small molecules or molecular fragments. However, band-like charge transport can be a key to high mobility in organic semiconductors. Charge and exciton migration is assisted by nuclear motion, and intra- and intermolecular vibronic interactions play an important role in the hopping process. Therefore, understanding how molecular structure and molecular packing affect charge and exciton localization and migration in organic semiconductors may help one in the design of high-mobility transport layers.

Multireference *ab initio* methods give a reliable tool for distinguishing between different localizations of charges or excitons, because they make it possible to treat equally important states on equal grounds. We propose a computational procedure based on CASSCF/XMCQDPT calculation to track the charge or exciton transfer path and to elucidate the role of hard and soft vibrational modes [1] in the hopping process. The examples of typical electron- and hole-transporting materials Bebq2 and α-NPD are considered [2, 3].

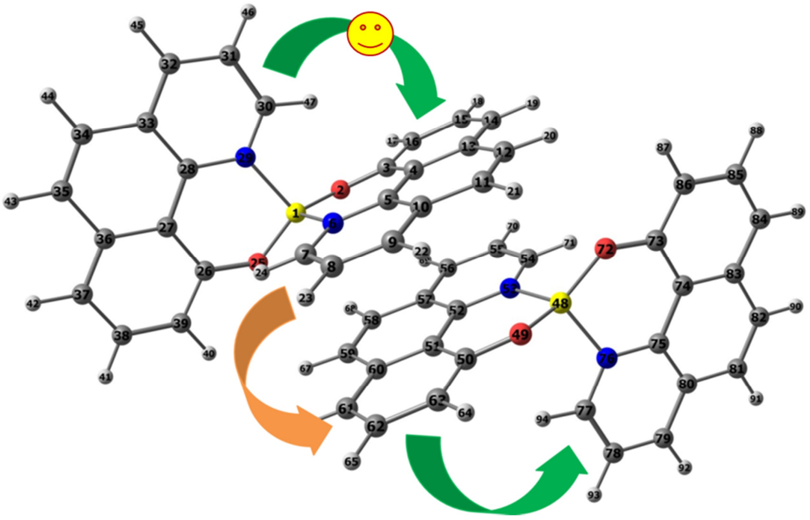

Figure 1: typical charge hopping process in a small-molecule organic semiconductor.

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Chalcogens Outerly and Innerly Functionalize Various Boron-Based Cages. Molecular Structures of the Resulting Heteroboranes Determined Using Electron Diffraction and Computational Protocols

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The development of modern computational methods, linked to improved methods for analysis of experimental gas-phase structural data, has allowed the stereochemistry of many boranes and heteroboranes to be determined with great accuracy over the past two decades. Many of these compounds have been prepared in the Institute of Inorganic Chemistry, Czech Academy of Sciences and gas-phase electron diffraction (GED) data have been obtained mainly at the University of Edinburgh and also at the University of Oslo and at the University of Bielefeld. Structural tools based on the concerted use of GED (using Edinburgh-based, Oslo-based, and Bielefeld-based refinement programs) and computations of the geometries and ^{11}B chemical shifts (*MOCED, SARACEN)* have been employed [1,2]. (^{11}B chemical shifts are often employed as an additional refinement condition.) Different *closo-* and *nido-*geometrical shapes containing sulfur and selenium are reported.

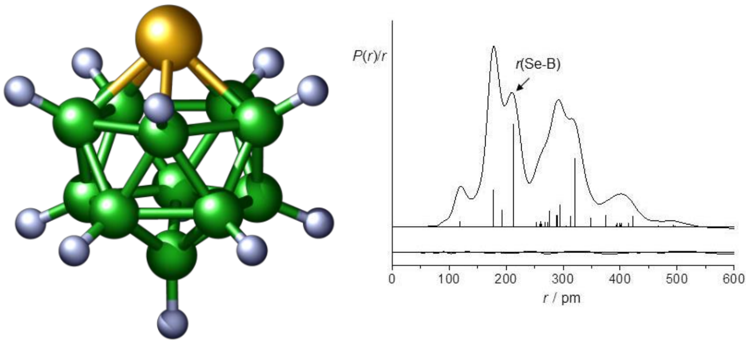

Figure 1: closo-1-SeB$_{11}$H$_{11}$, its molecular structure with radial distribution curve from GED as an example.

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Strategies and Requirements for the Automated Exploration of Complex Chemical Reaction Networks

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In recent years the computer based, automated exploration of reaction networks has seen a growing interest. A variety of different approaches have been proposed, implemented and used to explore a diverse set of chemical reactions[1–3].
All of these methods rely on a reasonably complete reaction network in order to allow for accurate predictions. A complete reaction network for a given area of interest consists of all thermodynamically relevant intermediates and all reaction paths that connect them. Already due to conformational diversity the reaction network generated for relatively simple chemical processes can be vast if they are to be complete.
The requirements for a software that strives to explore reaction networks in this manner will be highlighted using our own approach[4,5] as an example. Key steps in the exploration of networks, such as error control, as well as the final visualization and interpretation of generated data will be touched upon.

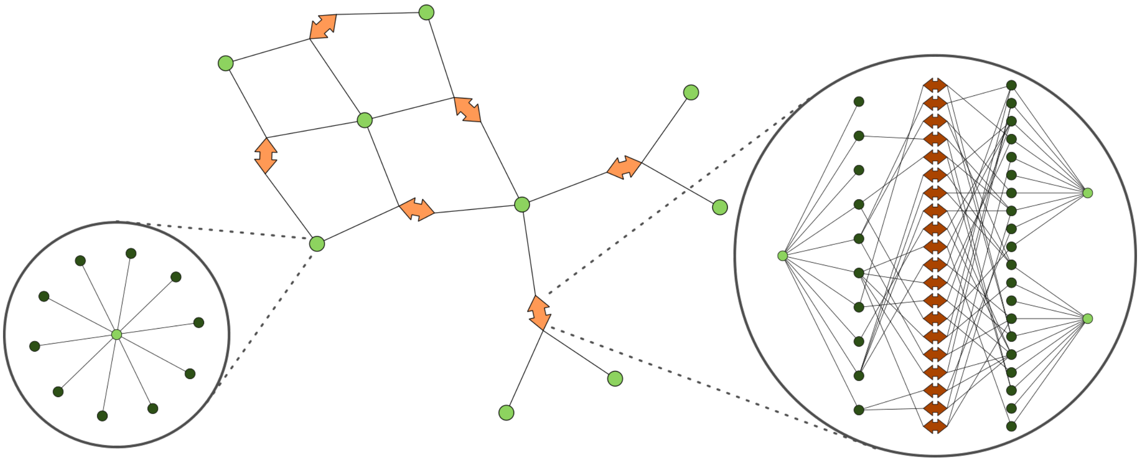

Figure 1: Example reaction network.

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Error-Propagation by Increments

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For many practical applications, it is crucial to know how large the error of a given quantum chemical method is [1]. Unfortunately, it is often not possible to compare to a reference calculation of high reliability, in particular for large molecules. To tackle this problem, we propose an approach based on the Bethe–Goldstone equation [2]. With this equation, any molecular property can be cast in terms of a many-body expansion, the bodies being fragments of the original molecule. Many popular approaches in quantum chemistry are based on this idea such as the method of increments [3], the kernel energy method [4], many-body expanded full configuration interaction [5], and the fragment molecular orbital method [6].

In our specific case, we do not rely on a fragmentation of the orbital space (as is done, for example, in the method of increments) but instead directly partition the molecular structure. Then, for each of the smaller fragments, a reliable but computationally demanding reference calculation is carried out (our approach is not tailored towards a specific method, but general enough to allow for any quantum chemical method). To be flexible with regard to the choice of fragmentation, it is often necessary to separate strongly interacting parts (*e.g.*, cutting through covalent bonds). We rely on the embedding approach proposed by Manby, Miller, and coworkers [7] to take such parts into account by a computationally less expensive method (see also Ref. [8]). It is found that our many-body expansion is quickly converging for the cases studied; in fact, it is often sufficient to truncate it at third order. Therefore, this method provides a viable way to reliably propagate errors calculated on smaller fragments to larger molecules [9].

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Understanding switchable processes in supramolecular systems

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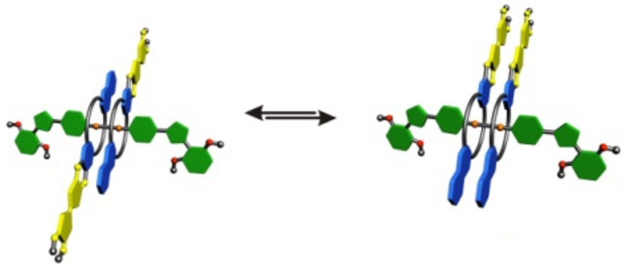
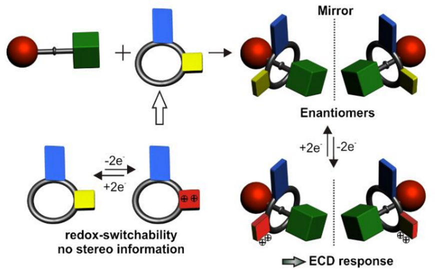
The 2016 Nobel prize in chemistry awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa "for the design and synthesis of molecular machines"[1] is proof of the broad interest in the creation of new supramolecular architectures capable of converting energy at the nanoscale. The nature of the underlying mechanisms of these "machines" are usually dominated by non-covalent interactions. As long as intermolecular interactions are the target, experimental approaches are often sufficient to obtain a satisfying understanding of the systems' properties. However, the mechanical bond between the different parts of a supramolecule converts most of the originally intermolecular interactions into intramolecular ones, presenting a great challenge for most experimental strategies. In these cases theoretical approaches are indispensable. Here, we study the intramolecular non-covalent interactions in two different kinds of rotaxanes functionalised by TTF (tetrathiafulvalene) units using DFT-based calculations to study and understand their switching mechanisms.



Switchable Co-conformation: A [3]rotaxane performs a controlled rotational motion stimulated by current in a CV setup.



Conformational chirality: A chirally active [2]rotaxane displays a charge-dependent CD signal reversal.

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1. The Nobel Prize in Chemistry 2016 *"for the design and synthesis of molecular machines"*, Royal Swedish Academy of Sciences.

Noncovalent Interactions of Boron Clusters

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Polyhedral boron clusters (boranes, boron hydrides) are large group of compounds with unique properties and unusual noncovalent interactions, which include dihydrogen bonds [1] and σ-hole interactions [2]. The counterintuitive ability of heteroboranes to form strong σ-hole interactions might be attributed to the multicenter bonding [3]. It breaks the classical electronegativity concept and results in areas of highly positive electrostatic potential (called σ-holes) on heteroatoms that are incorporated into the skeleton via multicenter type of bonding [3]. Group V, VI and VII elements in neutral heteroboranes can have highly positive σ-holes that are responsible for strong σ-hole interactions [2]. We have observed the S···π [4], Br···π [5], P···π [6] and Sb···H-B [7] types of σ-hole interactions of heteroboranes experimentally in the corresponding crystal packings.

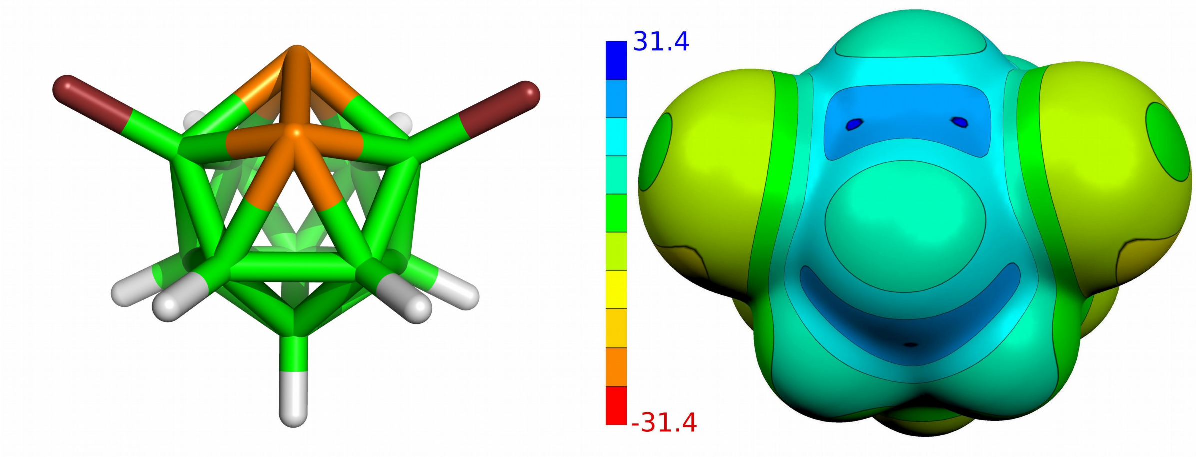

Figure 1: Molecular diagram (left) and electrostatic potential (right) on the 0.001 a.u. molecular surface of 3,6-Cl_2-closo-1,2-$P_2B_{10}H_8$. The ESP range in kcal mol^{-1}. Adopted from reference [6].

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Computational engineering of efficient enzyme catalysts for biodesulfurization of sour crude oil through 4S pathway

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In the last decades, the 4S metabolic pathway of bacterium *Rhodococcus erythropolis* strain IGTS8 has been discussed as an efficient and greener way to desulfurize organic sulfur compounds without degrading their carbon skeleton. This alternative is increadibly appealing as about 70% of the crude oil available worldwide is rich in organic sulfur compounds (mercaptans, thiols, sulfides, disulfides and thiophenes) that lead to high emissions of sulfur oxides (SO_X) after combustion, with repercussions in environment, health and industrial maintenance. More importantly, as regulatory agencies now demand for lower sulfur content fuels, we lack efficient methods to remove the abundant dibenzothiophene (DBT) and its alkylated derivatives. Two enzymes are referred to be the bottleneck of the 4S pathway: the $FMNH_2$-dependent monooxygenase DszC (k_{cat} = 1.6±0.3 min^{-1}, K_M = 1.4±0.3 μM) and the desulfinase DszB (k_{cat} = 1.7±0.2 min^{-1}, K_M = 1.3±0.3 μM).[1] Since the rate of the pathway has to be increased at least 500 fold to be of use in oil refining plants, we have been studying the reaction mechanism of these enzymes and attempted rational enzyme engineering protocols aiming at DszC and DszB, combining hybrid quantum mechanics/molecular mechanics methods and molecular dynamics simulations.[2-4]

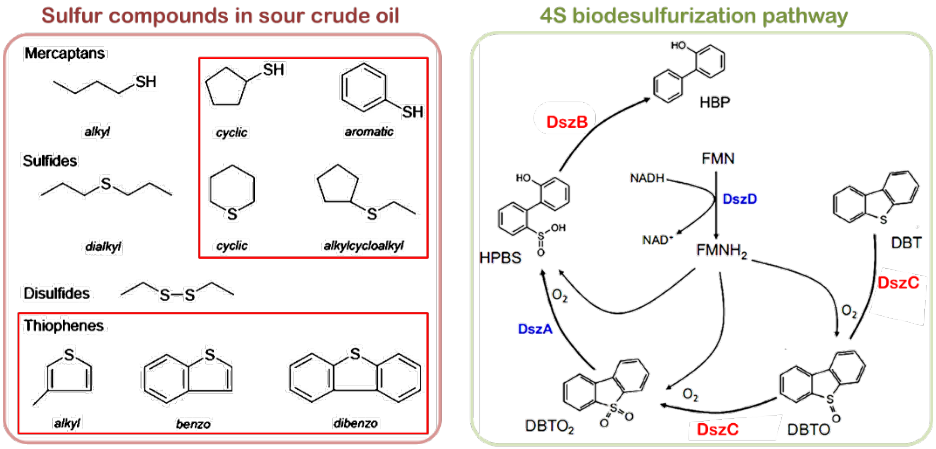

Figure 1: On the left, most common sulfur-containing organic molecules in sour crude oil, with the most abundant highlighted in red. On the right, depiction of 4S pathway, with the rate-limiting enzymes highlighted in red.

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Efficient quantum dynamics with the time-dependent density matrix renormalization group.

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Thanks to the design of increasingly more accurate ultrafast spectroscopic techniques, it is nowadays possible to resolve the dynamics of a molecule on the natural time scales of both its electronic and nuclear motions. The most accurate algorithms available in the literature to simulate molecular dynamics at the quantum level [1-2] rely on full configuration interaction (CI) expansions of the wave function. The exponential increase of the computational cost with the system size hinders, however, straightforward extensions to large molecular systems. This unfavorable scaling can be limited by expressing the wavefunction as a matrix product state, a parametrization employed in the well-known density matrix renormalization group algorithm (DMRG). The different strategies that have been designed to integrate the resulting equation of motion are broadly defined as time-dependent DMRG (TD-DMRG).

In the present contribution, we generalize a recently developed TD-DMRG algorithm [3] to electronic- [4] and vibrational-structure [5-6] quantum chemical Hamiltonians. We apply the resulting theory to simulate both the nuclear and electronic dynamics, possibly coupled together, of molecules with several dozens of degrees of freedom [7]. We assess the accuracy of the simulations by comparison with state-of-the-art experimental measurements obtained from time-resolved techniques. Moreover, we show that TD-DMRG outperforms its time-independent parallel in the calculation of high-order molecular properties and in the simulation of spectra in regions with a high density of excited states.

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A multiscale computational approach to investigate small gold nanoclusters optical features in solution

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Nowadays, the study of thiolate-protected gold nanoclusters is of the most promising research field in nanoscience. The intrinsic quantum confinement effects given by the small dimension of the metallic core, gives them unique chemical and physical properties. [1] Among all gold-based nanoclusters, $[Au_{25}(SR)_{18}]^q$ (R = organic ligand) received the most extensive attention because it was one of the first cases of fully resolved crystal structure, primarily with q=-1 and then for q=0. [2,3] Despite the optical features for the isolated systems were deeply studied both from an experimental and a theoretical point of view [4,5], a full characterization of the absorption features for the neutral form of the nanoclusters in terms of single-particles transitions were still lacking. Moreover, some recent studies demonstrate that the optical behavior of a nanoclusters group can be really different from those of isolated particles, when their reciprocal distance is small enough. [6,7] This evidence requires some computational efforts to explore the mechanism beyond these modifications and how can them be tuned. Thus, our work has the purposes of elucidate how the optical features of the $[Au_{25}(SR)_{18}]^0$ changes with respect to the charged form and to understand how different ligands can affect the equilibrium distances (and the optical features) of various nanoclusters in solution.

To achieve these results, Time Dependent Density Functional Theory (TDDFT) simulations were performed on two X-Ray Diffraction (XRD) resolved structures of $[Au_{25}(SCH_3)_{18}]^q$ finding that different orientations of the organic ligands (coming from different nanoclusters structures) gives different equilibrium geometries and a sensible modification of the inner metallic kernel structure and polarizability. However, these changes do not affect the computed optical absorption spectra, confirming that the organic ligand orientations, while creating measurable distortions of the core geometry, bring negligible effects on the nanoclusters optical properties, even though the excitations that are important for the lowest transitions are mainly localized on the gold core. Meanwhile, metadynamic simulations were performed on $[Au_{25}(SCH_2CH_3)_{18}]^0$, $[Au_{25}(SC_{16}H_{33})_{18}]^0$ and $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-1}$ double clusters systems, in dichloromethane, using as collective variable the center of mass of the two gold core. The results show a tendency in forming cluster aggregates in the long chain substituted nanoclusters system. Surprisingly, the Coulomb repulsion among nanoclusters in $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-1}$ system are well screened by the solvent and we recover a near cluster configuration minimum in the free energy profile. Finally, the free energy profile of the short chained nanoclusters pair is almost flat, indicating that no aggregations naturally occur here.

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Modulation of Single-Molecule Magnet Properties: a Theoretical Investigation

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In the beginning of the century, the emergence of lanthanide-based systems exhibiting slow relaxation of their magnetization opened a new chapter in the field of molecular magnetism.[1,2] These so called lanthanide-based Single-Molecule Magnets (SMMs) found many potential applications such as high-density data storage, spintronic or quantum computing.[3] On the computational point of view, the multiconfigurational wavefunction-based SA-CASSCF/RASSI-SO approach is known as a powerful tool to obtain a good description of both the electronic and magnetic features of lanthanide-based SMMs.[4] In this work, we will focus on the application of such computational protocol to describe the modulation of the SMM properties observed in two different recently characterized architectures. We will investigate the evolution of the relaxation mechanisms occuring in both an Er(III)-based polyoxometallate and an extended-tetrathiafulvalene Dy(III)-based dimer (see Figure) upon hydration/dehydration and reversible redox- and hydro-magnetic switching processes, respectively.

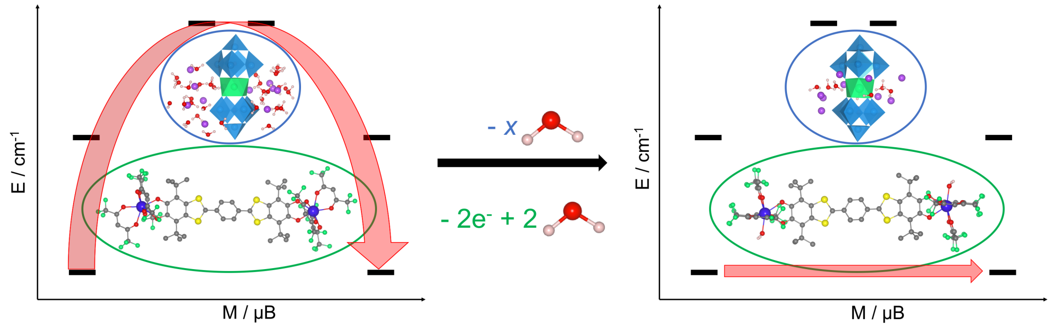

Figure: From slow (left) to fast (right) relaxation of the magnetization in the Er(III) (blue) and Dy(III) (green) systems.

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This laboratory is part of a project that has received funding from the European Research Council (ERC) under the European Unions Horizon 2020 research and innovation program (ERC-CoG MULTIPROSMM grant agreement N725184).

Theoretical Studies on the Hydroaminoalkylation of Alkenes with Primary and Secondary Amines

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Nowadays the industrial production of primary amines from alkenes requires two chemical transformations with an aldehyde as an intermediate. A waste-free alternative to this two-step process would be a hydroaminoalkylation of alkenes with methylamine. Current research results indicate that the α-alkylation of amines with alkenes catalyzed by early transition-metal complexes represents an efficient and atom economic method for the synthesis of functionalized amines from simple and easily available starting materials.[1] While the successful use of secondary amines, such as dimethylamine,[2] strongly underlines the enormous industrial potential of this reaction, the analogous intermolecular α-alkylation of primary amines, especially methylamine, remains an unsolved synthetic task to this day. Particularly worth mentioning is the fact that intramolecular α-alkylation, however, can be carried out with secondary and primary aminoalkenes.[3]

In this work, we present calculated thermodynamic data which explain these experimental findings for the first time. Based on the computed catalytic cycle several competing reactions are examined in more detail. It turns out that these are of crucial importance for the different behavior of primary and secondary amines. For these studies DFT-functionals in the program package Gaussian09.b01[4] were used.

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Water Oxidation on $WO_3(001)$ – An Embedded Cluster Study

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Photocatalytic water splitting is a cutting-edge topic nowadays since there is no environmental friendly and efficient way known for hydrogen production. Tungsten trioxide (WO_3) is a promising material for photoanodes due to its many advantages like the narrower band gap compared to TiO_2, which allows for absorption of a large portion of the solar spectrum. Furthermore, the deep valence band position makes the water oxidation thermodynamically easier and the high electrical conductivity leads to good electron transport properties [1,2].

The aim of this contribution is to understand the involved mechanism of the water oxidation process on an atomistic level. To achieve this, we use hybrid DFT calculations with periodic boundary conditions [3] and multiconfigurational methods in terms of CASSCF [4]. The latter allows for the calculation of specific excited states in the relevant degrees of freedom.

We present results of the oxidation process by studying both ground and charge transfer states using an embedded cluster model. These results provide a molecular view into the water oxidation process and can also be used for high-precision wave-packet quantum dynamics which will allow for new time-resolved insights.

Since the wave packet dynamics require a very dense grid of potential points and the high-dimensional potential energy surface exhibits a too complex topology that can no longer be mapped using analytical expressions, we utilize machine learning as fitting procedure [5]. Applying state-of-the-art methods like dropout [6] and residual connections [7] we achieve a much more accurate and topology-preserving fit than using conventional neural networks.

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Understanding the mechanism and regioselectivity of the copper and Ruthenium catalyzed 1,3-dipolar cycladdition of azido ribose derivative with alkyne. A DFT study

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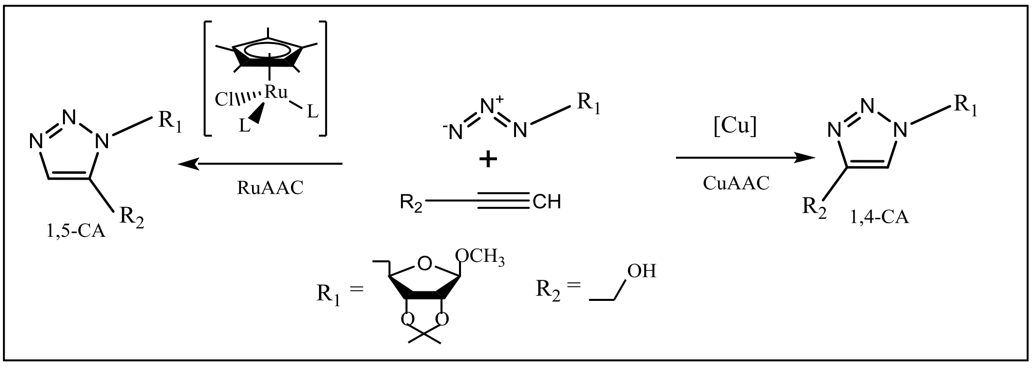
1,2,3 Triazoles constitute a family of compounds known for their momentous and valued biological activities. Their biomedical applications include the treatment of tumors, diabetes, microbial and fungal infections and inhibition of HIV protease.

Experimentally, the uncatalyzed cycloaddition of azido derivative of ribose with alkyne provides a mixture of 1,4- and 1,5-triazole regioisomers at higher temperature. Whereas, the Copper-catalyzed Azide−Alkyne Cycloaddition (CuAAC) gives only the 1,4-disubstituted triazole. Another discovery in the field of *click chemistry* reveals that the Ruthenium-Catalyzed Azide−Alkyne Cycloaddition (RuAAC) yields, exclusively, the 1,5-disubstituted triazole.

In the present work, both the uncatalyzed and the CuAAC and RuAAC reactions (***Scheme 1***) were modeled and discussed in terms of relative energies obtained from quantum-mechanical calculations performed at the B3LYP/6-31G(d) level of theory. For Cu(I), Ru(II) and Cl atoms, the LANL2DZ effective core potential has been used. In the absence of Cu(I) and Ru(II) catalysts, two regioisomeric reaction pathways were studied, indicating that the AAC reaction takes place through an asynchronous one-step mechanism. Coordination of Cu(I) to alkyne produces relevant changes in this AAC reaction as a consequence of the large enhancement in the nucleophilicity of the corresponding dinuclear Cu(I)-acetylide complex with formation of the experimentally observed 1,4-tiazole. Formation of the 1,5-tiazole via the RuAAC appears to proceed via oxidative coupling of the azide and alkyne reactants to give a six-membered ruthenacycle intermediate. The first carbon-nitrogen sigma bond is formed between the more electronegative carbon of the alkyne and the electrophilic terminal nitrogen of the azide. This step is followed by a reductive elimination yielding the formation of the final 1,5-triazole product.



Scheme 1

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Using effective QED potentials in molecular calculations

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Improvements in both computational power and methodology nowadays allow highly accurate electronic structure calculations including both relativistic and electron correlation effects. A next challenge for increased accuracy is the inclusion of the effects of quantum electrodynamics (QED), notably the electron self-energy and vacuum polarization, which in principle means going beyond the no-pair approximation [1,2].

Calculations within the rigorous QED framework are reported for few-electron systems, but this approach cannot be extended to many-electron systems because of the high computational cost. A more practical, but approximate approach is the introduction of effective potentials to incorporate QED effects. In the atomic case, some codes for the calculation with effective potentials are reported [3,4], and their application show that this approach leads to excellent agreement with experiment [5].

Meanwhile, in the case of molecules, the methods to incorporate QED effect are limited to pseudopotentials (e.g. [6,7]) and model potentials [8], which are obtained by parameter fitting. Although the former approach can describe the electronic structure of the valence orbitals well, they cannot calculate core-level properties and the disagreement with more elaborate potentials is non-negligible [5].

In this work, we report the first implementation of effective QED potentials in a program for all-electron 4-component relativistic calculations, DIRAC [9]. We have implemented three kinds of potentials: the Uehling potential [10] for vacuum polarization, Pekka and Zhao's model potential [8], and Flambaum and Ginges's effective potential for self-energy effects [11]. The one-electron integrals for these potentials are evaluated numerically, and are available for all electronic structure methods available in DIRAC. In our presentation, we show some results of sample calculations.

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Time-dependent Optimized Coupled-cluster Framework for Laser-driven Multielectron Dynamics

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The role of electron correlation [1] is of paramount importance in the theoretical study of laser-driven multielectron dynamics [2]. The multiconfiguration time-dependent Hartree-Fock (MCTDHF) method [3, 4] and time-dependent complete-active-space self-consistent-field (TD-CASSCF) method [5] serve best for the purpose. However, factorial computational cost prohibits large scale applications of these methods. By limiting the configuration interaction (CI) expansion of the wavefunction, a few other methods have been developed [6, 7] compromising the condition of size-extensivity. Therefore, the choice of the exponential coupled-cluster wavefunction as a replacement of the truncated CI wavefunction is a worthy proposal to restore the lost size-extensivity. Recently, we have derived and implemented a gauge invariant time-dependent optimized coupled-cluster (TD-OCC) method considering double and triple excitation amplitudes (TD-OCCDT) with optimized orthonormal orbitals, where both the orbitals and the amplitudes are time-dependent and propagated in time [8].

Additionally, we have implemented methods based on the further approximate coupled-cluster wavefunction in the TD-OCC framework namely time-dependent optimized coupled-electron pair approximation (TD-OCEPA) method and time-dependent optimized second-order many-body perturbation theory (TD-OMP2) to reach out larger chemical systems (See Fig.1, e.g.).

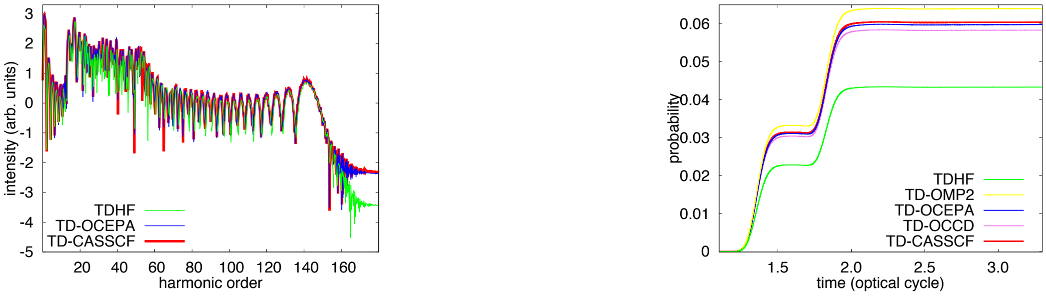

Fig. 1 High-order harmonic generation (HHG) spectra (left) and the time evolution of single ionization probablity (right) of Kr exposed to a laser pulse with a wavelength of 1500 nm and intensity of 1.8×10^{14} W/cm^2. Comparison of the results of TD-CASSCF, TD-OCCD, TD-OCEPA, TD-OMP2 and TDHF methods. All the correlated methods predict similar HHG spectra. Eight valence electrons are correlated among 13 active orbitals for the correlated methods.

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A Density-Based Basis Set Correction For Wave Function Theory

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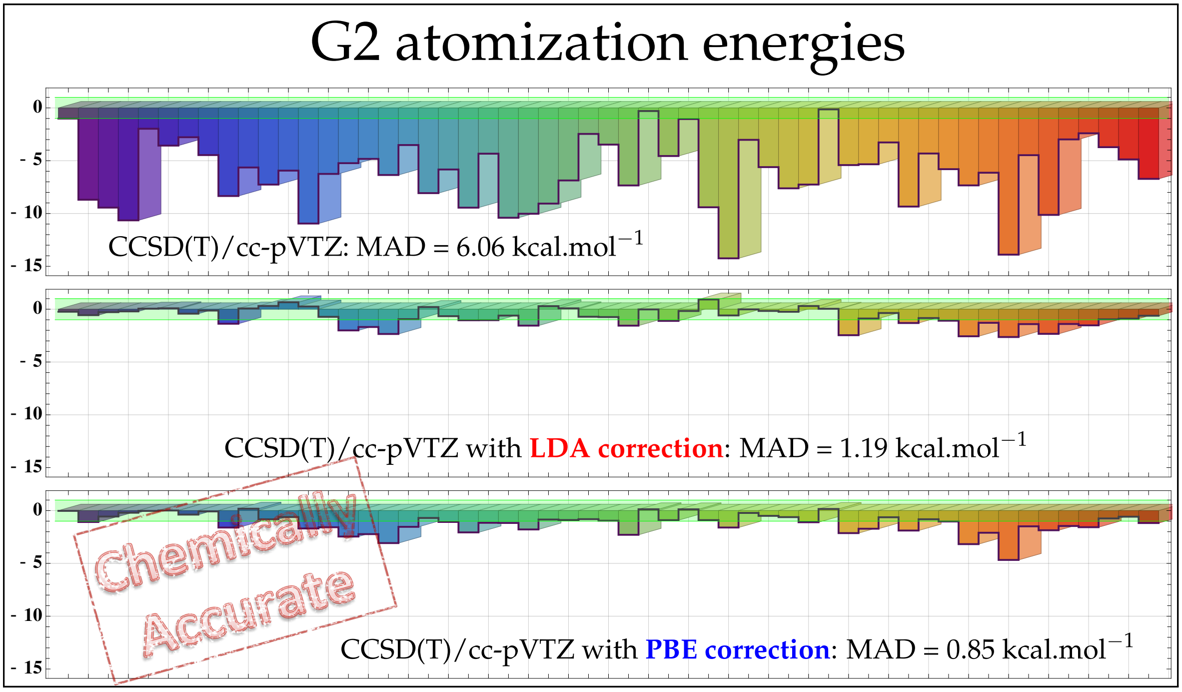
We report the extension of a recently proposed [1] universal density-based basis set incompleteness correction that can be applied to any wave function method, together with its first numerical application on molecular systems. The present correction, which appropriately vanishes in the complete basis set (CBS) limit, relies on short-range correlation density functionals (with multi-determinant reference) from range-separated density-functional theory (RS-DFT) to estimate the basis set incompleteness error. Contrary to conventional RS-DFT schemes which require an *ad hoc* range-separation *parameter* μ, the key ingredient here is a range-separation *function* $\mu(\mathbf{r})$ which automatically adapts to the spatial non-homogeneity of the basis set incompleteness error. As illustrative examples, we show how this density-based correction allows us to obtain CCSD(T) atomization and correlation energies near the CBS limit for the G2 set of molecules with compact Gaussian basis sets.



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Spin-orbit coupling from multistate CASPT2

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We report an approach to compute spin–orbit coupling within the extended multistate second-order multiconfigurational perturbation theory (XMS-CASPT2). Our approach is based on the state interaction method, in which both diagonal and off-diagonal elements of the spin–orbit matrix are computed at the CASPT2 level. It enables analysis of chemical processes that occur as a result of a change in spin multiplicity, such as photocatalysis and those involving intersystem crossing. The algorithm for this approach is being implemented in the BAGEL program package.

Poster: P2-122

Scaling relation between adsorption energies of oxygen reduction reaction intermediates at defective TiO_2 surfaces

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Enhancing the oxygen reduction reaction is a major topic of electrocatalysis research. The maximal enhancement is achieved, within the thermodynamic argument, by aligning the adsorption free energies of reaction intermediates so that energy barriers along the reaction path are minimized. Full alignment is, however, difficult to realize. This is due to the linear scaling relation between the adsorption energies of intermediates along the reaction path, which has been observed almost universally in electrocatalyst materials including Pt [1]. Thus, finding a way to deviate from this universal relation is an important issue in catalyst design.

Here, we investigate such possibility by studying TiO_2 surfaces modified with substitutional dopants or oxygen vacancies [2]. Defective oxide surfaces can provide various sites for the adsorption including the lattåice oxygen and metal sites as well as oxygen vacancies and impurity sites. Thus, the adsorption energies at the oxide surfaces are expected to deviate from the universal scaling because adsorbents can take various adsorbed structures.

Our density functional calculations suggest that the universal scaling is violated on TiO_2 particularly when the adsorbent forms bonding not only with a metal atom but also with a lattice oxygen atom (Figure 1). Most importantly, in this case, the perfect alignment of the adsorption free energies is possibly achieved. This fact suggests that TiO_2 has the potential to surpass conventional catalysts such as Pt in terms of oxygen reduction reaction activity.

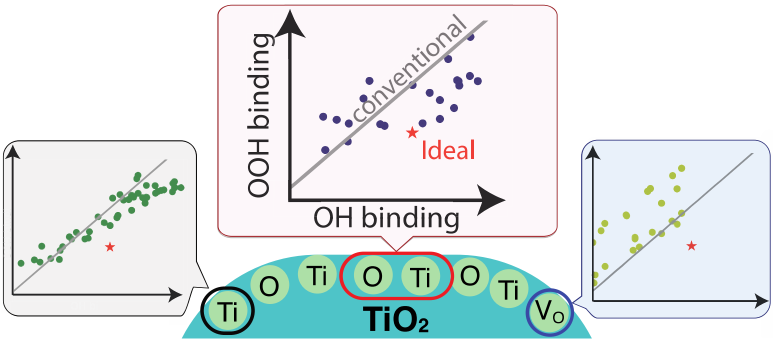

Figure 1. Correlation between adsorption energies of OH and OOH at various sites on TiO_2 surface

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Computational modelling of pH Responsive Nanovalves in Controlled-release System.

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ABSTRACT

A category of nanovalves system containing the cucurbit [7] uril ring on a stalk tethered to the pores of mesoporous silica nanoparticles (MSN) is theoretically and computationally modelled. This functions to control opening and blocking of the MSN pores for efficient targeted drug release system. Modelling of the nanovalves depend on the interaction between cucurbit [7] uril and the stalk in relation to pH variation. Protonation of the nitrogen atom on the stalk occur at acidic pH, leading to unsatisfactory host-guest interaction in the nanogate, hence there is dethreading. High required interaction energy and conformational change is theoretically established to drive the release of cucurbit [7] uril at a certain pH. The release was found to occur between pH 5-7 which agreed with reported experimental results.

Combined Theoretical and Experimental Study of Bisphenol A Photolysis

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Bisphenol A (BPA) is a chemical of the phenol class. The structural formula of BPA is shown in Fig. 1. The photolysis of BPA under the action of UV irradiation was studied. However, the mechanism of photodegradation is not fully understood. The photolysis of the neutral molecular form of BPA has been described in a join experimental and theoretical. Quantum-chemical methods using the theory of intramolecular photophysical processes have been used to interpret the spectral-luminescent properties of BPA in hexane and toluene, to establish the orbital nature of photodissociative states and the mechanism of C_5–C_8 and C_8–C_{11} bonds splitting. The effect of excitation energy on the efficiency of photoreactions has been found.

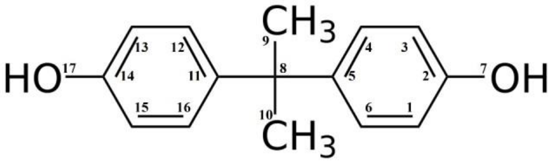

Figure 1: structure and atom numbering of BPA

The absorption and fluorescence spectra of BPA in hexane and toluene were recorded. The maximum of the long-wavelength absorption band of BPA in hexane is 274 nm (36496 cm^{-1}), in toluene – 282 nm (35461 cm^{-1}). These bands look broad to be from a single electronic transition. The theoretical studies were carried out using a software package based on the semi-empirical method INDO/s. It follows from the calculations that the long-wavelength band of the absorption spectrum is formed by three ππ*-type electronic transitions that are close in energy and intensity. During absorption, energy transfer occurs in the x and y planes with oscillator strengths of transitions of no more than 0.1. The breaking of C_5–C_8 and C_8–C_{11} bonds was calculated. When excited, the energy is localized on the bond to be broken due to the high value of the transition rate constant from the potential state curve S_1 (ππ*) to the photodissociative potential curve. The constants of nonradiative processes are calculated: the internal conversion at the $S_2(\pi\pi^*)\sim>S_1(\pi\pi^*)$ transition and the singlet-triplet conversion of $S_1(\pi\pi^*)\sim>T_9(\pi\sigma^*)$. The break of the C_8–C_{11} bond in the BPA molecule occurs with an increase in the bond length from 1.501Å to 1.801Å. The nonradiative transition between two states of the same multiplicity with an increase in coupling by $\Delta R = 0.3$Å is a fast process $S_2(\pi\pi^*)\sim>S_1(\pi\pi^*)$ with a rate constant of 10^{13} s^{-1}. Additionally, singlet-triplet crossing $S_1\sim>T_9$ region has been found. However, the rate constant was not great and was 10^8 s^{-1}. It has been shown that, when excited to the region of the long-wavelength absorption band, BPA photolysis occurs through the break of the C_8–C_{11} bond mainly by the mechanism of predissociation and is most effective in the singlet state of the πσ* type.

Financial support is acknowledged from projects 4.6027.2017/8.9 of the Russian Ministry and Program for improving the competitiveness (Tomsk State University, Tomsk, Russia).

Internal friction in protein systems: a physical insight from simplified models

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Origin of the internal friction in polymeric system is a long-lasting problem in physical chemistry and statistical physics, which can be traced back to de Gennes. During the recent decades, the contributions of the internal friction in protein systems are quantitatively measured based on protein dynamics. A series of theoretical studies were carried out to explore the possible mechanisms underlying these observations, but the origin of the internal friction is still not clear. In this work, we investigate the diffusion dynamics of a particle with interactions based on Langevin equation. It is observed that the conserved interaction may produce apparent effect on diffusion dynamics. This can be described based on certain projection on the energy landscape. This method is extended to the protein systems. The nonlinear dependence on the environmental viscosity and the dependence on the molecular topology are explained based on the Go-model. As a conclusion, a dynamic origin of the internal frictions is proposed, and the results successfully explain the observations related to protein systems. We believe this helps the understanding on the emergence of friction from conserved interactions in nature.

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Ab initio Calculations of the Rotational Spectrum of Hydroperoxy-acetaldehyde

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Peroxides are of great interest in atmospheric and combustion chemistry. They often play a major role in the radical portions of reaction networks under extreme conditions.
Peroxides pose challenges both experimentally and theoretically – their numerous conformers, instability and unusual structure make them difficult to detect, and complex behaviors such as tunneling complicate the theoretical structural calculations.

Peroxides produced from ozonolysis of alkenes are of particular importance. The simplest alkene, ethylene, is released into the atmosphere by plants and thus may react with atmospheric ozone to form a 5-membered ring, $c - C_2H_4O_3$. This, in turn, dissociates to form $CH_2 = O$ & $CH_2 = OO$, which subsequently fragments to $H, OH,$ and CO. A different possible path involves ring opening followed by H atom migration to produce $CHO - CH_2 - OOH$, hydroperoxy-acetaldehyde, a keto-hydroperoxide (KHP). This species was recently reported to be initially observed in a stirred jet system using VUV photoionization mass spectrometry [1]. We intend to detect KHP by chirped-pulse microwave spectroscopy, using high resolution microwave spectroscopy and a setup similar to Womack et. al. [2].

We predicted the rotational spectrum of the lowest lying conformer of KHP with high accuracy *ab initio* calculations. The geometry optimization was performed at the all-electron CCSD(T)/cc-pCVQZ level of theory, and anharmonic effects were incorporated through VPT2 calculations using the frozen core CCSD(T)/ANO0 level of theory. This structure (Figure 1) was found to have a hydrogen bond between the peroxy H atom and the carbonyl O atom, stabilizing it substantially compared to other conformers. MP2/ANO0 calculations showed that this conformer's energy is the lowest by at least $400\ cm^{-1}$ in comparison to other possible conformers.

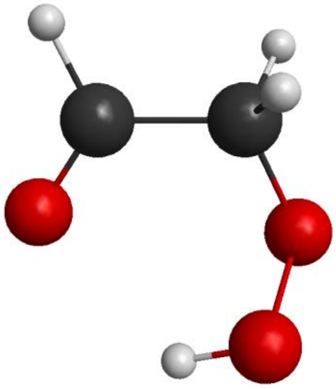

Figure 1. The calculated geometry of the most stable conformer of KHP

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Multilayer Approach to the IP-EOM-DLPNO-CCSD Method: Theory, Implementation, and Application

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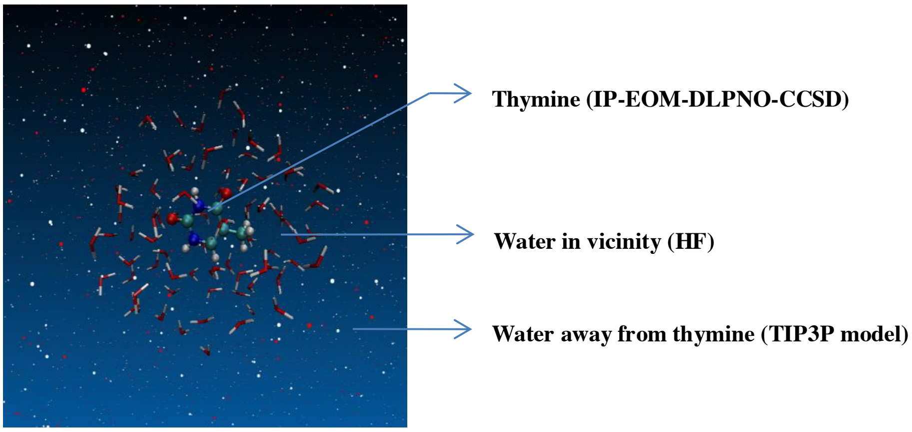

Three layer approach for studying the effect of bulk water on the IP & EA of Thymine

Many important chemical and biological processes take place in excited states. In the condensed phase, the surrounding environment plays a very crucial role in controlling and modulating such processes. However, a proper modeling of such environmental effects has always been a challenging task when it comes to the excited state instead of ground state as the excitation process involves a significant rearrangement of the wave function of the central fragment and the environment. We have developed a multi-layer scheme within the framework of EOM-CCSD method. The present scheme relies on the orbital localization to distinguish between different fragments within the system. The method is free from traditional problems of QM/MM method like over-polarization and cutting through the bonds. The resulting implementation is near black box and easy to use and is incorporated in a freely available quantum chemistry software. The accuracy and efficiency of the method is demonstrated by calculating ionization energies and electron affinities of solvated NABs, and DNA strand.

$$\hat{R}_k = \sum_{i,a} r_i^a \, a^+ i + \frac{1}{4} \sum_{i,j,a,b} r_{i_1 j_1}^{a_1 b_1} a_1^+ \, b_1^+ j_1 i_1$$

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Hybridization of Lipids to Monolayer and Bilayer Membranes of Triblock Copolymers[1]

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ABA triblock copolymers can exhibit two shapes in the membrane: bridge- and loop-conformations, leading to monolayer, bilayer, and mixed structures (Figure 1). The monolayer (bridge-conformation) and bilayer membranes (loop-conformation) were investigated by dissipative particle dynamics, and their hybridization with lipids was studied as well. The influence of the fraction of loop-conformation on the structural, mechanical, and transport properties of the membrane was obtained. The bilayer membrane is thicker than the monolayer membrane, and it is easier to stretch and bend. Moreover, the lateral diffusion and permeability of the former are greater than those of the later. Lipids can co-assemble with ABA copolymers into a hybrid membrane (Figure 1). A homogenous distribution of lipids in the membrane is acquired at low lipid concentrations (ϕ_l), but a lipid-rich domain emerges as $\phi_l > \phi_l^c$. The critical lipid concentration associated with phase separation is higher in the monolayer membrane, indicating that lipids prefer to hybridize with bridge-conformation rather than loop-conformation. In addition to the energy incompatibility, it is found that the structural incompatibility itself can lead to phase separation in hybrid membranes.

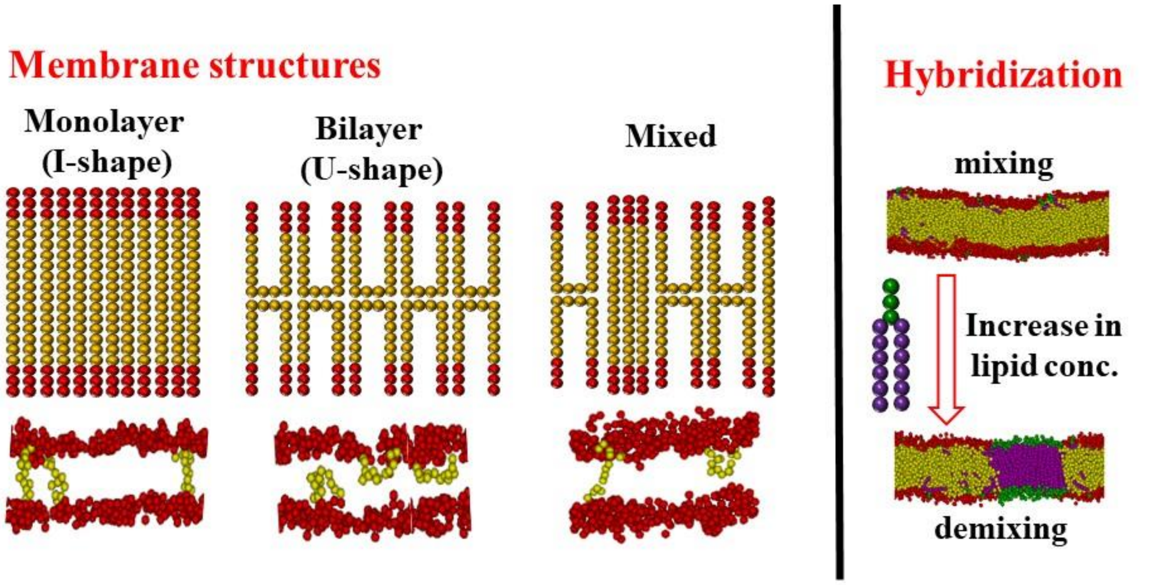

Figure 1: The schematic diagrams and snapshots of the monolayered, bilayered, and mixed membranes are shown. The snapshot of the hybrid lipid/ABA polymer membrane at different lipid concentration are demonstrated.

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Polarisation and response in Frozen Density Embedding

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The unfavourable scaling of accurate quantum-mechanical electronic structure methods makes them feasible only for small systems. This is a major hurdle for modelling real chemical systems such as molecules in an environment, be it a solvent, an enzyme, or a crystalline structure. Multi-level methods try to overcome this issue by using different levels of theory in different spatial regions, with consequent challenges in how to interface them.

Frozen Density Embedding Theory (FDET) [1] is a multi-level method which describes the effect of a frozen electron density of the environment, $\rho_B(\vec{r})$, on the wavefunction of the system of interest (Ψ_A), maintaining a quantum-mechanical description for the whole supermolecular system.

FDET exhibits large flexibility [2]: any choice of methods for the subsystems A and B is possible, including for instance the generation of $\rho_B(\vec{r})$ as a superposition of densities or time-averaging [3]. Additionally, the multi-level approach of this formalism can be further extended by combining it with other environment models (e.g. PCM, MM).

Three factors determine the accuracy of FDET-based embedded wavefunctions:

- the basis set expansion, which may excessively localise the wavefunction
- the approximate nature of the DFT functionals used for exchange-correlation and kinetic component of the interaction [4]
- violations of the condition $\rho_B^{frozen}(\vec{r}) \leq \rho_{TOT}^{I}(\vec{r})$

In particular, the latest relates to chemical phenomena such as polarisation and environment response.

In order to investigate the influence of such phenomena on the quality of FDET results, we selected embedding protocols which differ in the way $\rho_B(\vec{r})$ is generated, resulting in different manners of accounting for polarisation effects [5]. Via the application of such protocols to chemical systems with varying extent of polarisation and environment response, we aim to understand the sources of error in different types of interactions, and guide the selection of an appropriate protocol for the system at hand.

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Poster: P2-130

Charge transfer in mixed valence states: relaxation dynamics and transient absorption spectroscopy

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Quantum dynamical model calculations are performed on the photo-induced electron transfer in a mixed valence system interacting with different solvents. The simultaneously occuring processes of non-adiabatic population transfer and relaxation are studied in detail. Transient absorption traces, as recently recorded in our laboratory [1], are simulated, and the features of the spectra are related to the dynamics. The agreement with experiment hints at the fact that the employed one-dimensional models catch the essentials of the photochemistry of the investigated systems, and that it can be used for the interpretation of the transient-absorption spectra. It is inferred that the ultrafast electron-transfer processes take place on a sub-picosecond time scale and afterwards relaxation occurs within several picoseconds.

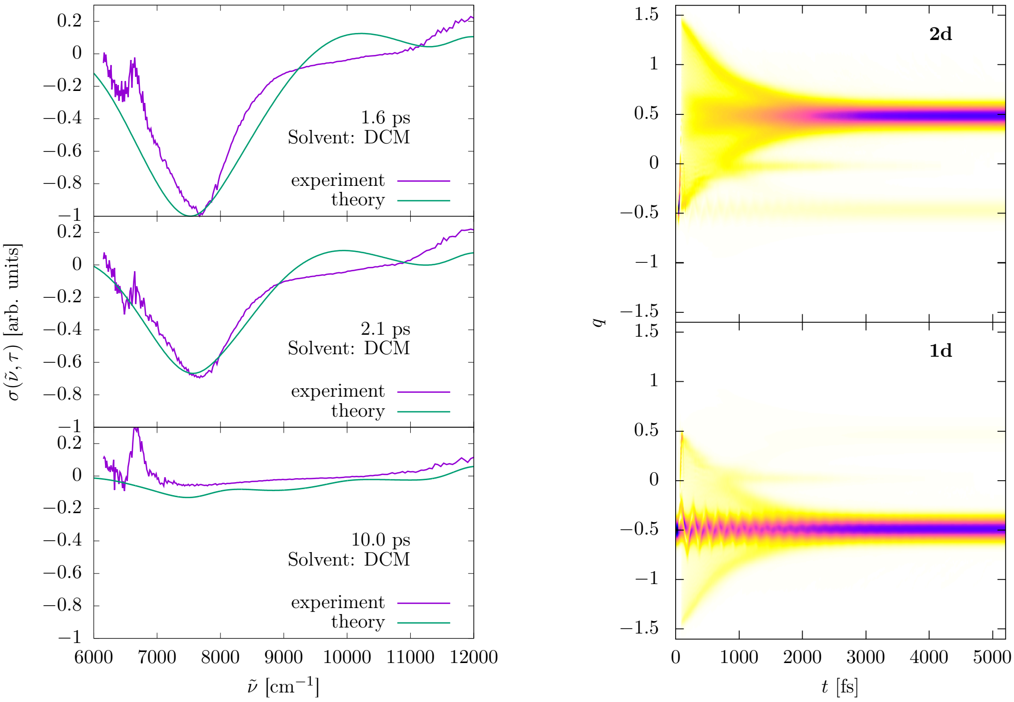

Figure 1: Comparison of measured and calculated spectra (left) and the wave-packet dynamics in the two diabatic states (1d, 2d) after laser excitation (right). Initially, only the 1d-state is populated.

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Water on rutile (110): A 5 dimensional wave packet dynamics study of photocatalysis

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Accurate and efficient high-dimensional wave packet dynamics are crucial for understanding quantum mechanical phenomena and receiving state resolved expectation values. Especially for photocatalytic reactions exact quantum dynamics are used to get insight into reaction pathways. High dimensional studies of large systems such as molecules on semiconductor surfaces require a lot of care to select the right parameters, which describe the system in its entirety but at the same time keep the demand on computational resources as low as possible. With high dimensional potential energy surfaces already existing for the system of H_2O on TiO_2 rutile (110) [1], we aim to study the dynamics of photodesorption and -dissociation of the water molecule in detail to gather knowledge about the mechanisms surrounding photocatalytic water splitting on titanium dioxide.

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Quantum Localization and Delocalization of Charge Carriers in Organic semiconducting Crystals

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Exciting new technologies such as organic light emitting diodes, photovoltaics and nanoelectronics rely on organic semiconductors. While important progress has been made in recent years towards theoretical and computational modelling of organic semiconductors (OSs), understanding the charge transport (CT) mechanism in these materials is still very challenging because the parameters determining the dynamics are typically outside the regime of validity of existing theories (e.g. Hopping or Band theories). On the other hand, non-adiabatic molecular dynamics simulations are in principle free of model assumptions permitting an "ab initio" view into the CT mechanism. We have recently developed an efficient decoherence-corrected surface hopping methodology (denoted FOB-SH) which allows us to propagate the coupled electron-nuclear motion in realistic condensed phase systems [1-3]. Here we present the first application of FOB-SH (blue symbols Fig 1) to the calculation of room temperature charge mobility for a series of eight molecular organic crystals. We obtain very good agreement with experimentally measured mobility values over three orders of magnitude successfully bridging the regime where hopping (green symbols) and band models (red symbols) are invalid as shown in Fig 1. We find that the mechanism of transport critically depends on the ratio between electronic coupling and reorganization energy (electron-phonon coupling), V/λ. At small ratios, as found in p-MSB and naphthalene, the charge carrier is delocalized over no more than 1-3 molecules and diffuses through the crystal via slow hopping. For values exceeding the critical threshold $V/\lambda > 1/2$ as found in pentacene and rubrene, the charge carrier forms a polaron delocalized over 10 or more molecules concomitant with a strong increase in mobility. Implications of our work for the search of new organic materials with high room temperature mobility will be discussed.

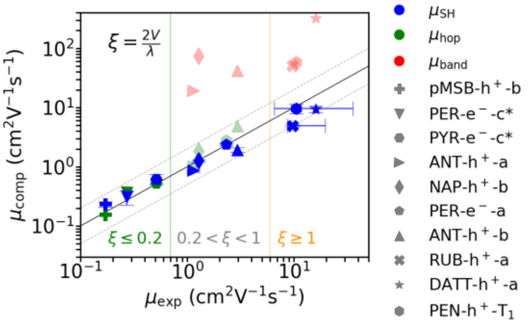

Figure 1: Comparison between computed and experimental (hole or electron) mobilities measured for eight organic semiconductors along different crystallographic directions. FOB-SH results are in blue, while hopping and band theory results are shown with green and red symbols respectively (shaded symbols represent regimes in which standard theories are no longer applicable).

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Structural characterization of the intrinsically disordered N-WASP domain V and its recognition by actin

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Intrinsically disordered proteins (IDP) are characterized by one or several regions which lack stable secondary and tertiary structure in their unbound state [1]. They frequently play crucial roles in the regulation of many biological processes and, to exert their functions, interact with several molecular partners. Formation of IDP-protein complexes can follow two limiting mechanisms, not necessarily exclusive [2]: the "induced fit" pathway, in which the disordered region binds to the protein partner and folded into an ordered structure on its surface, and the "conformational selection", in which the folded structure preexists in the IDP unbound state and is recognized by the protein partner. To gain insight into the structure and recognition mechanism of IDP-protein complexes, it is important to preliminary explore the conformational ensemble of IDP.

NMR experiments (CS and RDC) provide local information about their propensity to form transient secondary structures. On the other hand, small-angle X-ray scattering (SAXS) can deliver global information about their average size and shape. But, in order to infer a detailed conformational ensemble from NMR and SAXS data, it is most often necessary to use complementary *in silico* approaches to generate atomic scale structures, such as statistical coil generator or molecular dynamics (MD) simulations [3-7].

In the present study, we combined NMR, SAXS and *in silico* techniques to characterize the conformational ensemble of the fully disordered verprolin homology domain (V) of the Neural Wiskott-Aldrich Syndrome Protein (N-WASP), a pivotal protein in the regulation of the actin cytoskeleton dynamics [8]. Then, we used representative structure of the most populated clusters of its conformational ensemble to model the structure of N-WASP domain V in complex with actin.

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Mechanistic study of sulfur-poisoning and removal reactions of barium zirconate-based anodes: An ab initio atomistic calculation

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In the present study, we investigated the mechanism of sulfur-poisoning and removal reactions on the Y and Yb doped barium zirconate ($BaZrO_3$), the perovskite ceramic widely employed for solid oxide fuel cell (SOFC) application, by ab initio atomistic calculation. The computational result found that sulfur-poisoning reaction corresponds to SO_4^{2-} formation in the bulk phase, $H_2S_{(g)} + 6O^{2-}_{(b)} \rightarrow SO_4^{2-}{}_{(b)} + 2OH^-_{(b)} + 8e^-$. This oxidation reaction is a kinetically fast, with the highest activation barrier of 0.58 eV, and thermodynamically favorable process with the overall exothermicity of -17.21 eV, showing the vulnerability of $BaZrO_3$-based anodes. The poisoned SO_4^{2-} can be removed by the assistance of steam, in which SO_4^{2-} is oxidized to SO_2, $SO_4^{2-}{}_{(b)} + 2H_2O_{(g)} + 2e^- \rightarrow SO_{2(g)} + 4OH^-_{(b)}$. This reduction reaction is somewhat energetically unfavorable with the highest barrier of 1.81 eV and overall endothermicity of 0.79 eV. Additionally, we utilized the thermodynamic corrections on the energetic result to examine the effects of partial pressures of gas-phase species and applied voltage in the practical SOFC operation. Our result found that the poisoning reaction is unavoidable as the nonspontaneity occurs at rather high electric bias of -2.07 V or low H_2S contamination of 100 ppm. On the other hand, the removal reaction is feasible at the bias voltage of -0.31 V or sufficient steam partial pressure of 0.03 torr. The computationally resolved mechanisms provide the new insights for better design anodic materials in SOFC application and have been further confirmed by *operando* surface enhanced Raman spectroscopy (SERS).

How Argon Atom Affects the Vibrational Structure of Protonated Nitrogen Dimers?

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The effect of the argon messenger atom in the vibrational spectra of protonated N_2 dimers are theoretically investigated. A multilevel potential energy surface (PES) and dipole moment function (DMF) are constructed and used for the anharmonic vibrational frequency calculations. The $Ar_mN_4H^+$ (m=0-1) underwent a geometry optimization and normal mode calculations at the CCSD/aug-cc-pVDZ level of theory. Both linear form and T-shaped ArN_4H^+ were found to be the possible structures for the argon-tagged protonated N_2 dimers. That is, the vibrational frequencies of linear ArN_4H^+ and T-shaped ArN_4H^+ are calculated to reproduce the experimental action protonated N_2 dimer spectrum. All ab initio calculations were performed using the Gaussian 09 suite of programs. Comparison of the calculated spectrum for the bare N_4H^+ ion and Ar-tagged N_4H^+ ion reveal that the reduction of the symmetry group, from $D_{\infty h}$ to either $C_{\infty v}$ or C_{2v}, results to a richer vibrational structure in the 500 – 1700 cm^{-1} region. When compared with the previously reported action spectra [1], it appears that both position isomers for ArN_4H^+ are needed to account for the additional bands in the observed spectrum. These findings demonstrate the active role of the messenger atom in relaxing some of the selection rules for the bare ion – resulting to an augmentation of the bands in the action spectrum.

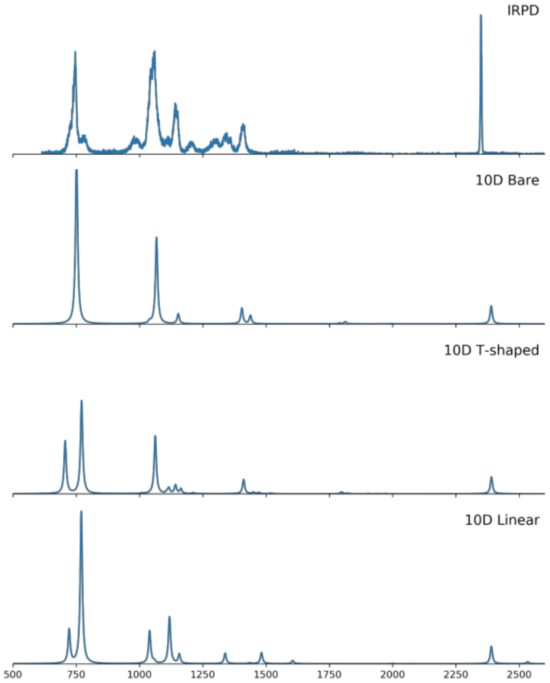

Figure 1: Infrared Photodissociation (IRPD) of ArN4H+ and calculated anharmonic spectrum for N_4H^+, ArN_4H^+ (T-shaped), and ArN_4H^+ (Linear).

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Termination Effects of Pt/*v*-$Ti_{n+1}C_nT_2$ MXene Surfaces for Oxygen Reduction Reaction Catalysis

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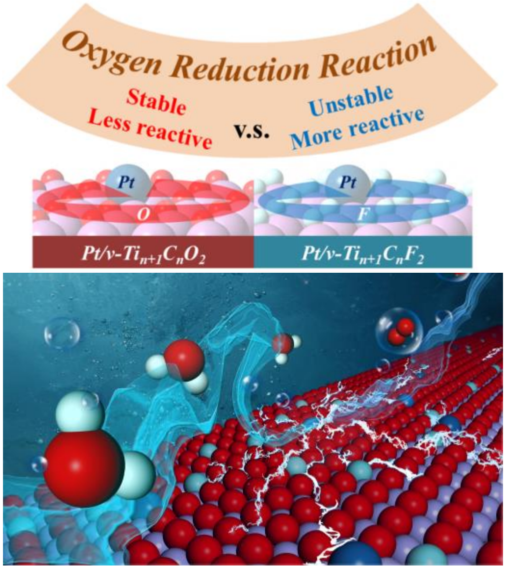
Ideal catalysts for the oxygen reduction reaction (ORR) have been searched and researched for decades with the goal to overcome the overpotential problem in proton exchange membrane fuel cells. A recent experimental study [1] reports the application of Pt nanoparticles on the newly discovered 2D material, MXene, with high stability and good performance in ORR. In this work, we simulate the $Ti_{n+1}C_nT_x$ and the Pt-decorated Pt/*v*-$Ti_{n+1}C_nT_x$ (n = 1−3, T = O and/or F) surfaces by first-principles calculations. We focus on the termination effects of MXene, which may be an important factor to enhance the performance of ORR. The properties of different surfaces are clarified by exhaustive computational analyses on the geometries, charges, and their electronic structures. The free-energy diagrams as well as the volcano plots for ORR are also calculated. On the basis of our results, the F-terminated surfaces are predicted to show a better performance for ORR but with a lower stability than the O-terminated counterparts, and the underlying mechanisms are investigated in detail. This study provides a better understanding of the electronic effect induced by the terminators and may inspire realizations of practical MXene systems for ORR catalysis.



Scheme1. The oxygen reduction reaction (ORR) on the Pt decorated O- and/or F-terminated MXene surfaces in an aqueous system.

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Finding Reaction Pathways with optimal atomic index mappings

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Finding complex reaction and transformation pathways, involving many intermediate states, is in general not possible on the DFT level with existing simulation methods due to the very large number of required energy and force evaluations. This is due to a large extent to the fact that for complex reactions, it is not possible to determine which atom in the educt is mapped onto which atom in the product. Trying out all possible atomic index mappings is not feasible because of the factorial increase in the number of possible mappings. By using a penalty function that is invariant under index permutations, we can bias the potential energy surface in such a way that it obtains the characteristics of a structure seeker whose global minimum is the product. By performing a Minima Hopping based global optimization on this biased potential energy surface we can rapidly find intermediate states that lead into the global minimum. Based on this information we can then extract the full reaction pathway. We first demonstrate for a benchmark system, namely LJ_{38} that our method allows to preferentially find intermediate states that are relevant for the lowest energy reaction pathway and that we therefore need a much smaller number of intermediate states than previous methods to find the lowest energy reaction pathway. Finally we apply the method to two real systems, C_{60} and $C_{20}H_{20}$ and show that the found reaction pathway contains valuable information on how the system can be synthesized.

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Application of *GW*-BSE theory to transition-metal complexes

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The Bethe-Salpeter equation (BSE) was initially derived in nuclear physics and later imported to the field of computational solid-state physics. Recently, it has been widespread for calculating molecular excitation energies and provided optimistic results in a variety of systems. The BSE formalism is very similar to the time-dependent density functional theory (TDDFT) in the language of linear response, and thus has the same scaling with respect to system size as TDDFT. However, BSE can be applied for description of excitations that are particularly problematic for TDDFT, e.g. excitations with charge-transfer character. The BSE approach has recently been implemented in our TURBOMOLE program using a resolution-of-the-identity (RI) approximation for all two-electron integrals that are required to solve the equation. Since BSE normally requires quasiparticle energies from preceding *GW* calculations as input, *GW* and BSE have often emerged together, which is known as the *GW*-BSE formalism. The performance of the BSE approach for the computation of singlet and triplet excitation energies of small molecules has been assessed with respect to the quasiparticle energies used in the BSE calculations. Here we present several examples of application of *GW*-BSE to transition-metal complexes.

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