54th Symposium on Theoretical Chemistry "Non-Covalent Interactions"

Conference Book

(including abstracts)



17.-20. September 2018, Halle (Saale)

https://stc2018.de/



Impressum

STC Organizing Team, 10.09.2018 Prof. Dr. Daniel Sebastiani

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Part I.

Conference Information

1. Information from A to Z

AGTC Meeting

The meeting of the "Arbeitsgemeinschaft Theoretische Chemie" (AGTC) will take place on Monday evening, 18:10–18:50, in the Auditorium Maximum (*Universitätsplatz 1*).

Airport

The Leipzig–Halle airport (LEJ) is very close to Halle (Saale). It can be reached from Halle main station with the S5 and S5X trains (direction: Zwickau) in 12 minutes. These trains go twice an hour.

Book of Abstracts

The book of abstract is included in the conference book *(this document)*, see page 53. As already practiced at the STC conferences of the last years, we do **not** offer printed copies of the conference book. If you would like to have a printed version, we recommend printing it before your travel to Halle.

Charging Mobile Devices

see Power

Child Care

We offer free child care during the conference (Monday morning until Thursday noon). If you are interested in our child care program, please contact us at your earliest convenience.

Coffee Breaks

All coffee breaks (*see schedule*) take place in the Auditorium Maximum (*Universitäts-platz 1*), next to the lecture hall. We offer coffee, tea, softdrinks, and a selection of cookies in each of the coffee breaks.

Conference Desk

The conference desk is located in the Melanchthonianum (*Universitätsplatz 9, room "Medienraum"*), close to the entrance. It will be continuously staffed from 15:00 to 20:00 on Sunday, from 9:00 to 18:00 on Monday till Wednesday, and from 9:00 till 14:00 on Thursday.

Conference Dinner

The conference dinner takes place on Wednesday, 19.09.2018, from 19:00 till 23:00 in the "Dormero Hotel Rotes Ross" (*Leipziger Straße 76*). You will require your name badge to enter. The food is for free, and standard drinks (beer, wine, softdrinks) are free until 22:00. Starting from 22:00, all drinks have to be paid.

Excursions

The excursions take place on Wednesday afternoon, starting at 15:00. All excursions are covered by the conference fee (*no additional cost*). Sign-in to the excursions is handled at the conference registration. The number of participants is limited for some excursions. Please pick one single "excursion ticket" at the conference desk. For a list of excursions, please see page 16.

Lunch

In your conference bag, you will receive lunch vouchers for Monday till Wednesday. These are valid in the "Harzmensa" (*Harz 41*) and include one meal (not including drinks/desserts) per day.

Medical Service

In case of medical emergencies, please immediately call phone number 112 for first aid. If you require less urgent medical aid, please contact the conference desk.

Participants

There are 291 participants registered for the STC 2018. You can find a list of participants on page 37.

Poster Sessions

The poster sessions will take place on Monday and Tuesday evening (19:00-22:00) in the Melanchthonianum (*Universitätsplatz 9*). We will offer a selection of alcoholic and non-alcoholic drinks as well as snacks ("belegte Brötchen") during both poster sessions. Posters with odd numbers are scheduled for session A on Monday; posters with even numbers will be presented in session B on Tuesday. Posters should be in A0 portrait format. Please put your poster to the wall during the afternoon before the session in which your poster is scheduled. Please take off your poster **at latest** in the morning after your session. Posters which are left at the wall at lunch time will be disposed without further notice.

Poster Slam

We will have a so-called "poster slam" directly before each poster session (*see schedule*), where every presenting author has the chance to advertise his or her poster to the full audience with a few words. This short presentation will have a length of 60 seconds per participant, and uses one single slide, which had to be handed in before the conference. 22 persons registered for the poster slam.

Power

For your convenience, we installed power distributor sockets in many different seat rows within the Audimax, where the lectures take place. Therefore, you will be able to charge your electronic devices during the talks. If you don't need electricity, please do not occupy the places close to the distributor sockets.

Public Transport

Halle (Saale) is a relatively small city, and the conference venue is located directly in the city center. Therefore, you will probably not need to use the public transport (*e. g.*, walking from the main station to the conference venue takes around 20 minutes). Otherwise, you should buy an "Einzelfahrkarte" for $2.30 \in$, which is valid for one hour within the whole city of Halle. Please note that there are frequent ticket controls in the trams.

Presentations

see Talks

Printing

We do not offer poster printing service for participants of the conference. As the conference center is located directly in the city center, there are several copy shops within a few hundred meters of the venue.

Registration

Registration takes place at the conference desk, which is located in the Melanchthonianum (*Universitätsplatz 9, room "Medienraum*"), close to the entrance. It will be staffed from 15:00 to 20:00 on Sunday, from 9:00 to 18:00 on Monday till Wednesday, and from 9:00 to 14:00 on Thursday.

Restaurants

As the conference center is located directly in the city center, there are plenty of restaurants within a few hundred meters of the venue. Some restaurants and bars which are suitable for larger groups of people are marked in the map on page 8.

Schedule

see page 9

Talks

The conference program includes 11 invited talks and 32 contributed talks, which were selected from over 100 applications. Please understand that we had to reject even some very promising talks due to the large interest. All talks take place in the Auditorium Maximum (*Universitätsplatz 1*). Invited talks are scheduled for 30 minutes talk and 10 minutes discussion (40 minutes in total). Contributed talks are scheduled for 15 minutes talk and 5 minutes discussion (20 minutes in total). Please strictly adhere to these maximum times.

Speakers please upload their talks to the presentation computer in the break before their session. Own laptops may be used if really required (connection via **HDMI only**). Audio playback is not possible.

Taxi Companies

Below, you find the phone numbers of some local taxi companies (without ranking):

Taxi Halle	+49345 525252
Taxi Wienecke	+49345 5200022
Taxi Kobsch	+49345 5606222
Taxi Peschke	+4934602 20754
Taxi Kremmer	+49345 5323452
Taxi Banse	+49345 5601982

Venue

see page 7

Weather Forecast

The 10-day weather forecast for Halle (Saale) indicates temperatures of above 20 $^{\circ}$ C and a low probability of precipitation during the conference. Sounds good. Consider bringing your swimsuit :-)

Welcome Reception

An informal welcome reception will take place on Sunday evening, 18:00-20:00, in the "Stadthaus" (*Marktplatz 2*). There, we offer sparkling wine, orange juice, and pretzels to all participants which already have arrived (*included in the conference fee*).

WLAN

In both the Audimax (where the lectures and coffee breaks take place) and the Melanchthonianum (where the poster sessions are located) you can use WLAN to access the internet. You can either use Eduroam or our conference network. For the latter, connect to the network "event-net", open your web browser, and enter user name "stc2018@uni-halle.de" and password "atxt2o3Z". Please note that the conference network is not encrypted and should not be used for sensitive data.

2. Program

2.1. Venue

The conference venue of the STC 2018 is located directly in the city center of Halle (Saale):

- The **lectures** and **coffee breaks** will take place in the "Auditorium Maximum" *("Audimax", Universitätsplatz 1)*.
- The **registration** and **poster sessions** will take place in the "Melanchthonianum", which is directly opposite to the Auditorium Maximum *(Universitätsplatz 9, room "Medienraum")*. There, also the **conference desk** can be found, which is continuously staffed from 15:00 to 20:00 on Sunday, from 9:00 to 18:00 on Monday till Wednesday, and from 9:00 till 14:00 on Thursday.
- The informal **welcome reception** on Sunday evening will take place in the "Stadthaus Halle" (*Marktplatz 2*).
- You will receive **lunch vouchers** for the "Harzmensa", which is located a few hundred meters north of the conference venue (*Harz 41*).
- The **conference dinner** will be located in the "Dormero Hotel Rotes Ross" (*Leipziger Straße 76*).

The map on the next page shows these places. There, also some restaurants and bars which are suitable for large groups of people are suggested.

You can find an interactive map on our conference homepage (section "Location & Travel"), where the above locations are highlighted by markers.

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https://stc2018.de/
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2.2. Schedule

Time Sunday 16.9.		Monday 17.9.	Tuesday 18.9.	Wednesday 19.9.	Thursday 20.9.
08:50 - 09:00		Opening			
09:00 - 09:40		I1 P. Jungwirth	Hellmann Award	I7 R. Mata	I10 G. Hummer
09:40 - 10:00		C1 J. P. Götze		C21 J. M. Westermayr	C27 A. Bande
10:00 - 10:20		C2 M. Wolter		C22 C. Wiebeler	C28 D. Picconi
10:20 - 10:50		Coffee Break	Coffee Break & "Sekt-Empfang"	Coffee Break	Coffee Break
10:50 - 11:10		I2	C10 T. Jagau	18	C29 F. Pauly
11:10 - 11:30		L. A. Nafie	C11 P. Pinski	R. Vuilleumier	C30 F. A. Bischoff
11:30 - 11:50		C3 D. Sidler	C12 M. Roemelt	C23 I. Barth	C31 D. Golze
11:50 - 12:10		C4 M. Springborg	C13 S. Stopkowicz	C24 H. Elgabarty	C32 D. R. Rehn
12:10 - 12:50					I11 A. Krylov
12:50 - 13:10		Lunch Break	Lunch Break	Lunch Break	Closing / Poster Prize
13:10 - 13:40					
13:40 - 14:20		I3 R. Ludwig	I5 M. Sulpizi	I9 T. Kühne	
14:20 - 14:40		C5 H. Bahmann	C14 G. Gryn'ova	C25 E. Caldeweyher	
14:40 - 15:00		C6 B. Hartke	C15 R. H. Henchman	C26 T. Weymuth	
15:00 - 15:30		Coffee Break	Coffee Break		
15:30 - 15:50		I4 D. Andrienko	I6 M. Thoss		
16:10 16:20		C7 M Hollström	C16 L M Mowos		
16:20 16:50	Registration	C? I Coorgo			
16:50 17:10		Co J. George		Excursions	
17:10 17:20		C9 K. Toriner	Coffee Break		
17:20 - 17:40		Coffee Break	C18 J. Wilhelm		
17:40 - 18:00		Poster Slam A	C19 G. Berghold		
<u>18:00 - 18:10</u> 18:10 - 18:20			C20 A. Blume		
18:20 - 18:50	Welcome	AGTC Meeting	Poster Slam B		
18:50 - 19:00	Neception				
19:00 - 20:00		Poster Session A	Poster Session B	Conference	
20:00 - 22:00		(odd numbers)	(even numbers)	Dinner	
22:00 - 23:00					

The author names are links to the list of participants. The contribution numbers and titles are links to the book of abstracts. Click to jump to the corresponding sections.

Sunday, 16. September 2018

15:00-20:00 Regist	ration (Melanchthonic	ınum, Universitätsplatz 9)
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18:00 – 20:00 Welcome Reception (Stadthaus, Marktplatz 2)

Monday, 17. September 2018

		Session Chair:	Daniel Sebastiani
8:50-9:00	Ope	ning	
9:00-9:40	I1	Pavel Jungwirth	Exploring Solvated Electrons by Explosive as well as Non-Explosive Experiments and Simulations
9:40 - 10:00	C1	Jan Philipp Götze	QM/QM Models of a Molecular Mechanism Controlling Photoprotective Quenching in Higher Plants
10:00 - 10:20	C2	Mario Wolter	Improved Partitioning of Biomolecules for Quantum-Chemical Embedding Calculations Based on Graph Theory

10:20-10:50 Coffee Break

		Session Chair:	Daniel Sebastiani
10:50-11:30	I2	Laurence Nafie	Chirality and Electron Transition Current Density in Molecular Vibrations: VCD and ROA
11:30-11:50	C3	Dominik Sidler	Beyond Rosenfeld Equation: Computation of Vibrational Circular Dichroism Spectra for Anisotropic Solutions
11:50-12:10	C4	Michael Springborg	On the Theoretical Optimization of Properties

^{12:10-13:40} Lunch Break

		Session Chair	: Pavel Jungwirth
13:40 - 14:20	I3	Ralf Ludwig	Competing Interactions in Ionic Liquids: When Cooperative Hydrogen Bonding Overcomes Coulomb Repulsion Between Ions of Like Charge
14:20-14:40	C5	Hilke Bahmann	Hybrid Exchange Density Functionals within the Local Range Separation Scheme
14:40 - 15:00	C6	Bernd Hartke	Global Geometry Optimization of Molecular Assemblies on Surfaces

15:00–15:30 Coffee Break

Session Chair: Pavel Jungwirth				
15:30-16:10	I4	Denis Andrienko	Molecular Understanding of Organic-organic Interfaces and Mixtures	
16:10-16:30	C7	Matti Hellström	Proton Transfer Mechanisms in Basic Solutions and at the Oxide/Water Interface Revealed by Neural Networks	
16:30-16:50	C8	Janine George	Ab Initio Anisotropic Displacement Parameters of Molecular Crystals	
16:50-17:10	C9	Ralf Tonner	Strain and Non-covalent Interactions as Driving Forces for Surface Reactivity	

17:10–17:40 Coffee Break

17:40-18:10	Poster Slam A

18:10-18:50 AGTC Meeting

19:00-22:00 Poster Session A (odd numbers)

Tuesday, 18. September 2018

:	Session Chairs:	Leticia González & Christian Ochsenfeld
9:00-9:40	Hellmann Aw	ard
9:40-10:20	Hückel Award	1

10:20 – 10:50 Coffee Break & "Sekt-Empfang"

Session Chair: Ricardo Mata				
10:50-11:10	C10	Thomas Jagau	Coupled-Cluster Treatment of Molecular Strong-Field Ionization	
11:10-11:30	C11	Peter Pinski	Analytical Gradient for a Pair Natural Orbital-based Local MP2 Method, and for Faster Double-hybrid Density Functional Geometry Optimizations	
11:30-11:50	C12	Michael Roemelt	On the Importance of Choosing an Adequate Active Space for Large-Scale Multireference Calculations	
11:50-12:10	C13	Stella Stopkowicz	Closed-shell Paramagnetism Revisited: A Low-field Effect Due to a Strong-field Three-state Avoided Crossing	

12:10-13:40 Lunch Break

Session Chair: Ralf Ludwig			
13:40-14:20	15	I5 Marialore Sulpizi Water at Interfaces: Structure and Vibrational Spectroscopy from ab in Simulations	
14:20-14:40	C14	Ganna Gryn'ova	Conceptual Framework of Molecular Electronics
14:40-15:00	C15	Richard Henchman	Hierarchical Method to Determine the Entropy of Molecular Systems

15:00 – 15:30 Coffee Break

Session Chair: Ralf Ludwig			
15:30-16:10	I6	Michael Thoss	Electron Transport in Molecular Junctions
16:10-16:30	C16	Jan-Michael Mewes	Twist and Shine: Organic TADF Emerges from the Interplay of Non-covalent Interactions, Triplet-exciton Delocalization, and Post Franck-Condon Effects
16:30-16:50	C17	Wolfgang Quapp	Simple Models for Mechanochemistry

16:50–17:20 Coffee Break

		Session Chair:	Daniel Sebastiani
17:20-17:40	C18	Jan Wilhelm	Applying Quantum Chemistry to Reactivity in the Condensed Phase
17:40 - 18:00	C19	Gerd Berghold	Digital Finance at Deutsche Bahn AG
18:00 - 18:20	C20	Alfred Blume	History of Chemistry in Halle
18:20 - 18:50	Poste	r Slam B	

19:00 – 22:00 Poster Session B (even numbers)

Wednesday, 19. September 2018

Session Chair: Michael Thoss			
9:00-9:40	17	Ricardo Mata	Non-covalent Interactions: from Gas Phase Benchmarks to Communication in Enzymes
9:40-10:00	C21	Julia Maria Westermayr	Neural Networks Trained on Ab-initio Data for Executing Surface Hopping Molecular Dynamics
10:00 - 10:20	C22	Christian Wiebeler	Structural Basis of the Red/Green Spectral Tuning in the Cyanobacteriochrome Slr1393

10:20 – 10:50 Coffee Break

Session Chair: Michael Thoss			
10:50-11:30	18	Rodolphe Vuilleumier	Vibrational Circular Dichroism Spectra From First-Principle Molecular Dynamics Simulations
11:30-11:50	C23	Ingo Barth	Non-zero Electron Current Densities for the Vibrating Hydrogen Molecular Ion in a Single Electronic Born-Oppenheimer Ground State
11:50-12:10	C24	Hossam Elgabarty	The Mechanism of Overhauser Dynamie Nuclear Polarization in Insulating Solids

12:10-13:40 Lunch Break

Session Chair: Anna Krylov			
13:40-14:20	I9	Thomas Kühne	Teaching New Tricks to an Old Dog to Quantify the Degree of Covalency of Hydrogen Bonding
14:20 - 14:40	C25	Eike Caldeweyher	DFT-D4: An Accurate and Generally Applicable Tight-binding Based Dispersion Correction for Density Functional Theory
14:40 - 15:00	C26	Thomas Weymuth	Statistical Analysis of Semiclassical Dispersion Corrections

15:00-19:00 Excursions

19:00 – 23:00 Conference Dinner (Dormero Hotel "Rotes Ross", Leipziger Straße 76)

Please note:

- You will need your name badge to enter.
- The food is for free.
- Standard drinks (beer, wine, softdrinks) are free from 19:00 to 22:00. Starting from 22:00, all drinks have to be paid.

Thursday, 20. September 2018

Session Chair: Thomas Kühne			
9:00-9:40	I10	Gerhard Hummer	Molecular simulations of lipid membrane sensing
9:40-10:00	C27	Annika Bande	Can You Do More? – Yes! Quantum Dot Inter-Coulombic Decay with Three Electrons
10:00 - 10:20	C28	David Picconi	Photodynamics and Spectroscopy of Halogens Embedded in Rare Gas Solids. Quantum Dynamical Description of the I ₂ :Kr system

10:20 – 10:50 Coffee Break

Session Chair: Thomas Kühne			
10:50-11:10	C29	Fabian Pauly	Robust Periodic Fock Exchange with Atom-centered Gaussian Basis Sets
11:10-11:30	C30	Florian Bischoff	The Accurate Computation of Molecular Properties Using Multiresolution Analysis
11:30-11:50	C31	Dorothea Golze	Accurate Core-level Spectra from GW: An Efficient Approach within a Localized Basis
11:50-12:10	C32	Dirk Rehn	Inelastic X-ray scattering amplitudes in the ADC/ISR framework
12:10-12:50	I11	Anna Krylov	Solvent Effects in Core- and Valence-level Photoionization Spectroscopy

12:50-13:10 Closing & Poster Prize

2.3. Excursions

On Wednesday afternoon, we offer the following excursions to participants of our conference. All of these excursions are fully covered by the conference fee (*no additional cost*). The sign-in to the excursions will be managed at the conference desk. Please pick one single "excursion ticket" at registration time.

• Visit to "Leopoldina"

Founded in 1652, the Leopoldina is the oldest scientific learned society in Germany, and even the oldest continuously existing national science academy of the world. We offer a guided tour through the building.

• Visit to "Landesmuseum für Vorgeschichte"

The State Museum of Prehistory in Halle (Saale) is the archaeological museum of the German state of Saxony–Anhalt. Its collection, comprising more than 15 million items, is among the most extensive and important in Germany. We offer a guided tour through the museum.

• Visit to "Franckesche Stiftungen"

The Francke Foundations (Franckesche Stiftungen) were founded in 1695 as a Christian, social and educational work by August Hermann Francke. Francke Foundations are today a modern educational cosmos closely connected with their history. The Francke Foundations are on the German proposal list as a UNESCO World Heritage Site since 1999. We offer a guided tour through the foundations.

• Guided city tour

Within 2 hours, a good survey of the historical city and the related facts is given.

• Hike along the Saale river with a view over Halle

The hike will have a length of around 5 km, and will lead over a hill directly at the Saale river, from where you will have a view over Halle. The Hike ends at the "Peißnitzhaus" (*Peißnitzinsel 4*), where a picnic at the Saale shore is anticipated (depending on the weather). Probably you can buy some food and drinks at the Peißnitzhaus, but it is better to bring your own stuff. It is another 2 km walk from Peißnitzhaus back to the conference venue.

On our conference homepage, you will find internet links with additional information to some of these locations (see section "Program" and scroll down to "Excursions"):

https://stc2018.de/

3. List of Talks / Posters

3.1. List of Invited Talks

I1	Jungwirth, P.	Exploring Solvated Electrons by Explosive as well as Non-Explosive Experiments and Simulations
I2	Nafie, L.	Chirality and Electron Transition Current Density in Molecular Vibrations: VCD and ROA
13	Ludwig, R.; Knorr, A.; Niemann, T.; Neumann, J.; Paschek, D.	Competing Interactions in Ionic Liquids: When Cooperative Hydrogen Bonding Overcomes Coulomb Repulsion Between Ions of Like Charge
I4	Andrienko, D.	Molecular Understanding of Organic-organic Interfaces and Mixtures
15	Sulpizi, M.	Water at Interfaces: Structure and Vibrational Spectroscopy from ab initio Simulations
I6	Thoss, M.	Electron Transport in Molecular Junctions
I7	Mata, R.	Non-covalent Interactions: from Gas Phase Benchmarks to Communication in Enzymes
18	Vuilleumier, R.; Scherrer, A.; Jähnigen, S.; Sebastiani, D.	Vibrational Circular Dichroism Spectra From First-Principle Molecular Dynamics Simulations
19	Kühne, T.	Teaching New Tricks to an Old Dog to Quantify the Degree of Covalency of Hydrogen Bonding
I10	Hummer, G.	Molecular simulations of lipid membrane sensing
I11	Krylov, A.	Solvent Effects in Core- and Valence-level Photoionization Spectroscopy

3.2. List of Contributed Talks

C1	Götze, J. P.; Ostroumov, E. E.; Reus, M.; Holzwarth, A. R.	QM/QM Models of a Molecular Mechanism Controlling Photoprotective Quenching in Higher Plants
C2	Wolter, M.; Looz, M. V.; Meyerhenke, H.; Jacob, C. R.	Improved Partitioning of Biomolecules for Quantum-Chemical Embedding Calculations Based on Graph Theory
C3	Sidler, D.; Bleiziffer, P.; Riniker, S.	Beyond Rosenfeld Equation: Computation of Vibrational Circular Dichroism Spectra for Anisotropic Solutions
C4	Springborg, M.	On the Theoretical Optimization of Properties
C5	Bahmann, H.; Klawohn, S.	Hybrid Exchange Density Functionals within the Local Range Separation Scheme
C6	Hartke, B.; Freibert, A.; Dieterich, J. M.	Global Geometry Optimization of Molecular Assemblies on Surfaces
C7	Hellström, M.; Quaranta, V.; Behler, J.	Proton Transfer Mechanisms in Basic Solutions and at the Oxide/Water Interface Revealed by Neural Networks
C8	George, J.; Englert, U.; Dronskowski, R.	Ab Initio Anisotropic Displacement Parameters of Molecular Crystals
С9	Tonner, R.; Pecher, L.	Strain and Non-covalent Interactions as Driving Forces for Surface Reactivity
C10	Jagau, T.	Coupled-Cluster Treatment of Molecular Strong-Field Ionization
C11	Pinski, P.; Neese, F.	Analytical Gradient for a Pair Natural Orbital-based Local MP2 Method, and for Faster Double-hybrid Density Functional Geometry Optimizations

C12	Roemelt, M.; Khedkar, A.; Krewald, V.; Pantazis, D.	On the Importance of Choosing an Adequate Active Space for Large-Scale Multireference Calculations
C13	Stopkowicz, S.; Borgoo, A. B.; Hampe, F. H.; Tellgren, E. I. T.; Klopper, W. K.; Gauss, J. G.; Teale, A. M. T.; Helgaker, T. H.	Closed-shell Paramagnetism Revisited: A Low-field Effect Due to a Strong-field Three-state Avoided Crossing
C14	Gryn'ova, G.; Corminboeuf, C.	Conceptual Framework of Molecular Electronics
C15	Henchman, R.; Higham, J.; Chakravorty, A.; Gräter, F.	Hierarchical Method to Determine the Entropy of Molecular Systems
C16	Mewes, JM.	Twist and Shine: Organic TADF Emerges from the Interplay of Non-covalent Interactions, Triplet-exciton Delocalization, and Post Franck-Condon Effects
C17	Quapp, W.; Bofill, J. M.; Ribas-Arino, J.	Simple Models for Mechanochemistry
C18	Wilhelm, J.; Deglmann, P.	Applying Quantum Chemistry to Reactivity in the Condensed Phase
C19	Berghold, G.	Digital Finance at Deutsche Bahn AG
C20	Blume, A.	History of Chemistry in Halle
C21	Westermayr, J. M.; González, L.; Marquetand, P.	Neural Networks Trained on Ab-initio Data for Executing Surface Hopping Molecular Dynamics
C22	Wiebeler, C.; Rao, A. G.; Schapiro, I.	Structural Basis of the Red/Green Spectral Tuning in the Cyanobacteriochrome Slr1393
C23	Barth, I.; Renziehausen, K.; AlBaraghtheh, T.	Non-zero Electron Current Densities for the Vibrating Hydrogen Molecular Ion in a Single Electronic Born-Oppenheimer Ground State

C24	Elgabarty, H.	The Mechanism of Overhauser Dynamie Nuclear Polarization in Insulating Solids
C25	Caldeweyher, E.; Ehlert, S.; Grimme, S.	DFT-D4: An Accurate and Generally Applicable Tight-binding Based Dispersion Correction for Density Functional Theory
C26	Weymuth, T.; Proppe, J.; Reiher, M.	Statistical Analysis of Semiclassical Dispersion Corrections
C27	Bande, A.; Langkabel, F.	Can You Do More? – Yes! Quantum Dot Inter-Coulombic Decay with Three Electrons
C28	Picconi, D.; Cina, J. A.; Burghardt, I.	Photodynamics and Spectroscopy of Halogens Embedded in Rare Gas Solids. Quantum Dynamical Description of the I_2 :Kr system
C29	Pauly, F.; Irmler, A.; Burow, A. M.	Robust Periodic Fock Exchange with Atom-centered Gaussian Basis Sets
C30	Bischoff, F.	The Accurate Computation of Molecular Properties Using Multiresolution Analysis
C31	Golze, D.; Rinke, P.	Accurate Core-level Spectra from GW: An Efficient Approach within a Localized Basis
C32	Rehn, D.; Dreuw, A.; Norman, P.	Inelastic X-ray scattering amplitudes in the ADC/ISR framework

3.3. List of Posters – Session A

P1	Paul, S.; Das, S.	Hydrotrope-Assisted Solubilization of Sparingly Soluble Drug Molecules in Water
P3	de Wergifosse, M.; Grimme, S.	Nonlinear-Response Properties in a Simplified Time-Dependent Density Functional Theory (sTD-DFT) Framework: Evaluation of the First Hyperpolarizability
Р5	Höfener, S.	Biological Applications from Coupled Cluster Frozen Density Embedding
P7	Ehrmaier, J.; Domcke, W.; Sobolewski, A. L.	A Theoretically Conceived Photochemical Pathway to Solar Water Splitting Using Carbon Nitride Chromophores
Р9	Welsch, R.	Ring-Polymer Molecular Dynamics for Photochemistry
P11	Goerigk, L.	What We can Learn from Comprehensive Benchmark Studies: Insights for Method Developers and Users
P13	Gupta, P. K.; Daru, J.; Schienbein, P.; Marx, D.	What Can We Learn about the Solvation of Ions in Bulk Water by Studying Ion-water Clusters as a Function of Cluster Size?
P15	Schran, C.; Behler, J.; Marx, D.	Neural Network Potentials for Solvation: Protonated Water Clusters in Superfluid Helium
P17	Kloditz, R.; Radoske, T.; Patzschke, M.; Stumpf, T.	Bonding and Stability Analysis of Tetravalent f-Element Complexes with Mixed N-, O-donor Ligands
P19	Kraus, P.; Obenchain, D. A.; Frank, I.	Why Does my Back hurt: A Systematic Study of OCS Complexes
P21	Nizovtsev, A.; Korolkov, V. V.; Svatek, S. A.; Kerfoot, J.; Summerfield, A.; Besley, N. A.; Beton, P. H.; Besley, E.	Modelling the Structural and Optical Properties of Supramolecular Arrays Adsorbed on Hexagonal Boron Nitride: The Effect of Non-covalent Interactions

P23	Melani, G.; Nagata, Y. N.; Wirth, J. W.; Saalfrank, P. S.	Vibrational Spectroscopy and Dynamics of the Hydroxylated α -Al ₂ O ₃ (0001) Surface with (and without) Water: Insights from Ab Initio Molecular Dynamics
P25	Black, J.; Köhn, A.	Linear and Quadratic icMRCC Approximations
P27	Awad, M.; Atlam, F.	The Master Factors Influencing the Potancy of BACE-1 Alzheimer Inhibitors: Computational and Molecular Docking Studies
P29	Alizadeh Sanati, D.; Andrae, D.	Low-lying Electronic States of the Molecules AB_n (A = Sc – Ni, B = Cu/Ag/Au, $n = 1,2$)
P31	Peláez, D.; Kopec, S.; Panadés-Barrueta, R. L.	On the automatic computation of global intermolecular potential energy surfaces for non-covalently bound systems
P33	Proppe, J.; Gugler, S.; Reiher, M.	Dispersion-Corrected Noncovalent Interaction Energies from a Hybrid First-Principles–Gaussian Process Model
P35	Oncak, M.; Bersenkowitsch, N. K.; Heller, J.; Linde, C. V. D.; Beyer, M. K.	Photochemistry of Organic Molecules in Ionic Environment: Experimental-Theoretical Investigation of Aerosol Models
P37	Muñoz-Santiburcio, D.	Proton-irradiated Ice: Electronic Excitations via Real-Time TDDFT
P39	Zahn, S.	Deep Eutectic Solvents: Similia Similibus Solvuntur?
P41	Iron, M.	Taking Advantage of Host-Guest Interactions to Make the Undetectable Detectable in $^{19}{\rm F}~{\rm NMR}$
P43	Weingart, O.; Dokukina, I.; Dombrowski, D.; Pieri, E.; Ferré, N.; Nenov, A.; Garavelli, M.	QM/MM Photodynamics of Retinal Proteins with the OMx-MRCI Method
P45	Kabbe, G.; Dreßler, C.; Sebastiani, D.	Proton Mobility in Aqueous Systems: Combining ab-initio Accuracy with Millisecond Timescales
P47	Weber, F.; Ren, J.; Petit, T.; Bande, A.	Local XA Spectroscopy: A Database Approach to Carbogenic Materials

P49	Witte, F.; Schröder, H. V.; Schalley, C. A.; Paulus, B.	Non-covalent Interactions in Switchable Supramolecular Systems
P51	Gowdini, E.; Kharazian, B.; Hadipour, N.	A Study of Interaction between Au Nanoparticles and Some Nanoscale Surfaces
P53	Pototschnig, J.; Auer, A. A.	Revisiting the Canonical Product Format for Full Configuration Interaction
P55	Luy, JN.; Tonner, R.	Si(001) Defects and Their Impact on Surface Reactivity
P57	Stauch, T.; Ganoe, B.; Lee, J.; Epifanovsky, E.; Bennett, K.; Martin, M.; Head-Gordon, T.; Head-Gordon, M.	Accurate Calculation of NMR Properties with Wave Function Based Methods
P59	Schaupp, T.; Albert, J.; Engel, V.	Time-dependent Electron Momenta from Born-oppenheimer Calculations
P61	Gawrilow, M.; Suhm, M. A.	Ester-assisted Folding of Linear Alkyl Chains – a Combined Raman and Quantum Chemistry Approach
P63	Behnle, S.; Fink, R. F.	REMP: A New Hybrid Perturbation Theory with Improved Prediction Capabilities
P65	Ehlert, S.; Caldewehyer, E.; Grimme, S.	Application and Benchmarking of the New DFT-D4 Method
P67	Polly, R.; , B. S.; Vozarova, N.; Platte, T.; Finck, N.; Geckeis, H.	Incorporation of Radionuclides in Green Rust
P69	Mück-Lichtenfeld, C.; Cheng, Y.; Studer, A.	Boron-Boron One-Electron Bond in an Intermediate of the 1,2-Carbaboration of Unactivated Alkenes
P71	Diekmann, M.; Berger, R.	Theoretical Study of Rotational Spectra of Chiral Systems
P73	Kumar, N.; Marx, D.	Pressure-induced Effects on Self-cleavage Reaction of Ribozyme Catalysis: A Molecular Dynamics Study

P75	Pracht, P.; Grimme, S.; Bannwarth, C.; Dohm, S.; Hansen, A.; Pisarek, J.; Seibert, J.; Neese, F.	Fully Automated Quantum-Chemistry-Based Computation of Spin-Spin-Coupled Nuclear Magnetic Resonance Spectra
P77	Kelterer, AM.; Amorati, R.	Peroxyl Radical Reaction in Water: the Phenol Case
P79	Brieuc, F.; Schran, C.; Marx, D.	Converged Path Integral Simulations of Reactive Molecules down to Ultralow Temperatures at Coupled Cluster Accuracy
P81	Weinreich, J.; Römer, A.; Paleico, M. L.; Behler, J.	High-Dimensional Neural Network Potential for the Copper-Zinc System
P83	Mewes, JM.; Schwerdtfeger, P. S.	What is the Aggregate State of Super-heavy Copernicium at Ambient Conditions?
P85	Schattenberg, C. J.; Maier, T. M.; Kaupp, M.	Lessons from the Spin-polarization / Spin-contamination Dilemma of Transition-metal Hyperfine Couplings for the Construction of New Functionals
P87	Schmitt-Monreal, D.; Jacob, C.	Energies of Molecular Crystals from Many Body Expansion embedded in fully self-consistent Frozen Density
P89	Suhm, M.; Gottschalk, H. C.; Mata, R. A.	Benchmarking Non-covalent Interactions with Vibrational Spectroscopy
P91	Bursch, M.; McCrea-Hendrick, M. L.; Gullett, K. L.; Maurer, L. R.; Fettinger, J. C.; Grimme, S.; Power, P. P.	Counterintuitive Interligand Angles in the Diaryls $E\{C_6H_3-2,6-(C_6H_2-2,4,6-{}^iPr_3)_2\}_2(E = Ge, Sn, or Pb)$ and Related Species: The Role of London Dispersion Forces
P93	Schnabel, J.; Köhn, A.	Photoassociation Processes of Rb_3 and Kernel Based Methods for Generating Global Potential Energy Surfaces
P95	Lorenz, T.; Baburin, I. A.; Kamphausen, N.; Jäger, A.; Breitkopf, C.	A Theoretical Study of Gas Hydrates

P97	Hernández Vera, M.; Jagau, TC.	Implementation of the Resolution of the Identity Approximation for Complex Scaled Basis Sets
P99	Donati, L.; Keller, B. G.	Girsanov Reweighting for Metadynamics
P101	Welzel, M.; Jacob, C. R.	Complex Scaling for One-dimensional Model Systems
P103	Poidevin, C.; Auer, A. A.	Electronic Structure Calculation in Electrochemistry - Pt Nanoparticles on Carbon and Electrochemical Potential
P105	Böckmann, M.; Doltsinis, N. L.	Photomigration in Azo-polymer Thin Films Studied by Atomistic MD Simulations
P107	Heßelmann, A.	Study of a Molecular Torsion Balance in Solution
P109	Glasbrenner, M.; Vogler, S.; Ochsenfeld, C.	Electronic g-Tensors with Density Functional Theory: Study of the Gauge-origin Dependence and Sub-linear Scaling Implementation
P111	Bönisch, S.; Grau, B. W.; Tsogoeva, S. B.; Görling, A.	DFT Study on the Thermodynamics and Kinetics of a Novel Organocatalysed Five-step One-pot Synthesis
P113	Schwermann, C.; Doltsinis, N. L.	Computational Design of NHC-based Molecular Ratchets
P115	Spicher, S.; Bannwarth, C.; Ehlert, S.; Grimme, S.	GFN2-xTB: An extended Tight-Binding Quantum Chemical Method for Structures, Frequencies and Noncovalent Interactions across the Periodic Table
P117	Kunkel, M.; Bold, B. M.; Höfener, S.; Kranz, J. J.; Kleinekathöfer, U.; Elstner, M.	Benchmark and Application of LC-DFTB on the Fenna-Matthews-Olson Complex
P119	Wondrousch, D.; Schüürmann, G.	Complex Formation Trends of Ligand Binding toward $\mathrm{In^{3+}}$ and $\mathrm{Ge^{4+}}$
P121	Klahr, K.; Neugebauer, J.	Geometry Optimizations in a Subsystem DFT Formalism - A Structural Benchmark Study
P123	Ozen, A. S.; Dedeoglu, B.; Monari, A.; Etienne, T.; Aviyente, V.	Effect of Noncovalent Interactions on the Fluorescence Quenching Mechanism of Polymeric Sensors with Nitroaromatic Explosives

P125	Karbalaei Khani, S.; Hättig, C.	UV Absorption and Magnetic Circular Dichroism Spectra for PurinicNucleobases in Aqueous Solution at COSMO-RI-CC2
P127	Mattiat, J.; Luber, S.	Efficient Calculation of Raman Spectra and Excitation Profiles with Real-time propagation
P129	Kubisiak, P.; Eilmes, A.	Molecular Dynamics Simulations of Ionic Liquid Based Electrolytes for Na-Ion Batteries: Effects of Force Field
P131	Hoppe, H.; Eisfeld, W.	Development of a Relativistic Diabatic Potential Model for the Treatment of the Nonadiabatic Photodissociation of Iodobenzene
P133	Schmitz, K.; Grimme, S.; Bohle, F.	Automated Computation of Nuclear Magnetic Resonance Spectra
P135	Schmitz, S.; Seibert, J.; Pisarek, J.; Bannwarth, C.; Grimme, S.	Extension of the Element Parameter Set for Ultra Fast Excitation Spectra Calculation (sTDA-xTB)
P137	Brünink, D.; Doltsinis, N.	Optimization of Phosporescent Platinum(II) Complexes on Solid Substrates
P139	Schmitz, G.; Christiansen, O.	Benchmarking of Machine Learning Algorithms in the Context of Constructing Potential Energy Surfaces
P143	Berg, M.; Martínez-Mesa, A.; Uranga-Piña, L.; Bande, A.	Interparticle Coulombic Decay in Paired Quantum Dots: Exact Two-electron Dynamics vs. One-electron Dynamics on Coupled Effective Potentials
P145	Kehry, M.; Klopper, W. M.	Ab initio Computation of Förster Resonance Energy Transfer
P147	Massolle, A.; Neugebauer, J.	A new DFT Approach to Spin Densities and Exchange Coupling Constants for Polyradical Systems
P149	Khokhlov, D.; Belov, A.	Exciton Coupling in Chlorophyll-lutein Heterodimer of LHCII Photoantenna is Significantly Affected by the Size of MCSCF Space for Lutein Calculation
P151	Bargholz, A.; Köhn, A.	Excited States with Second Order Approximate Internally-contracted Multireference Coupled-cluster Linear Response Theory

P153	Atamas, N.; Bardik, V. Y.	Diffusion in Ionic Liquids – Alcohol Soulutions
P155	Scholz, R.; Saalfrank, P.; Lončarić, I.; Tremblay, J. C.; Füchsel, G.; Floß, G.	Multi-dimensional Femtosecond-laser Induced Dynamics of CO on Metals: Accounting for Electronic Friction and Surface Motion with Combined Models
P157	Alessio, M.; Sauer, J.	Chemically Accurate Energy Calculation for Molecule-Surface Interactions
P159	Barton, D.; Lao, K. U.; DiStasio Jr., R. A.; Tkatchenko, A.	The Tkatchenko-Scheffler and Many-Body Dispersion Methods: Implementation, Validation and Reproducibility in Electronic Structure Codes
P161	Kopec, S.; Martínez-Núñez, E.; Soto, J.; Peláez, D.	vdW-TSSCDS: An Automated Procedure for the Computation of Stationary Points on Intermolecular Potential Energy Surfaces
P163	Venghaus, F.; Eisfeld, W.	Isotropic Sampling for the Accurate Representation of Bound Potential Energy Surfaces
P165	Jähnigen, S.; Scherrer, A.; Vuilleumier, R.; Sebastiani, D.	Chiral Crystal Packing Induces Enhancement of Vibrational Circular Dichroism
P167	Loebnitz, M.; Dinkelbach, F.; Marian, C. M.	Intersystem-Crossing and Luminescence Properties of Triarylboranes
P169	Helmich-Paris, B.	Optical Properties of Open-shell Molecules with CASSCF Response Theory
P171	Partovi-Azar, P.; Hoefling, A.; Nguyen, D. T.; Sebastiani, D.; Theato, P.; Song, SW.; Lee, Y. J.	Structural Evolution of Sulfur-Copolymer Cathodes in Lithium-Sulfur Batteries Studied by Theoretical and Experimental NMR Spectroscopy
P173	Wuttke, A.; Mata, R. A.	Improving the Stability of EDA with Local Orbital Spaces
P175	Allaberdiev, K.	The Intermolecular Hydrogen Bond in <i>p</i> -substituted <i>o</i> -(N-diethyl)aminomethylphenols: Combined a DFT, QTAIM and ELF Investigation

P177	Zhang, S.; Schüürmann, G.	Regioselective B ₁₂ -Catalyzed Aromatic Dehalogenation Predicted by Density Functional Theory
P179	Khazaei, S.; Sebastiani, D.	Rotational Tunneling of Coupled Methyl Quantum Rotors: Single Rotor Potential Versus Coupling Interaction
P181	Scarbath-Evers, L. K.; Todorovic, M.; Golze, D.; Hammer, R.; Widdra, W.; Rinke, P.; Sebastiani, D.	Oligomers on Nanostructured Surfaces: Adsorption-induced Alteration of the Surface Reconstruction
P183	Ghafarian Shirazi, R.; Bistonni, G.; Neese, F.; Pantazis, D. A.	Differential Spin State Stabilization of Carbenes by Hydrogen and Halogen Bonding: a DLPNO Coupled Cluster Study

3.4. List of Posters – Session B

P2	Azriel, V.; Rusin, L. Y.	Trajectory Simulation of the Reverse Processes of a Recombination of the Ions which are Formed at Collision Dissociation of Two Neutral Molecules
P4	Brandenburg, G.	On the Physisorption of Water on Graphene: Sub-chemical Accuracy from Many-body Electronic Structure Methods
P6	Sathe, R.; Kumar, T. J. D.	Metal Functionalized [2,2]Paracyclophane and BN-substituted [2,2]Paracyclophane for Hydrogen Storage in Energy Application
Р8	Stein, M.; Escorcia, A. M.	QM/MM Investigation of the Functional Role of a Second Coordination Shell Arginine Residue in [NiFe]-Hydrogenases
P10	Bistoni, G.; Lu, Q.; Altun, A.; Yepes, D.	Local Coupled Cluster Theory Applied to Honcovalent Interactions in Real Life Chemistry. From Numbers to Chemical Insights
P12	Fransson, T.; Dreuw, A.	X-ray Emission Spectroscopy in the Algebraic-diagrammatic Construction Framework
P14	Daru, J.; Gupta, P.; Marx, D.	Restricting Solvation to Two Dimensions: Soft-landing Microsolvated Ions on Inert Surfaces
P16	Holzer, C.; Klopper, W.	Using the GW/BSE Scheme to Describe van der Waals Interactions
P18	Manz, J.; Grohmann, T.; Haase, D.; Jia, D.; Yang, Y.	Quantum Effects on the Structures and Dynamics of Small Cyclic Molecular Rotors Imposed by the Molecular Symmetry Group
P20	Wedig, U.; Nuss, J.; Xie, W.; Yordanov, P.; Bruin, J.; Hübner, R.; Weidenkaff, A.; Takagi, H.	Hierarchical Bonding Pattern in the Thermoelectric Material $Ag_6Ge_{10}P_{12}$

P22	Füchsel, G.	Steps in Heterogeneous Catalysis and Their Anomalous Role in the Dissociation of D_2 on Copper Surfaces
P24	Müller, F.; Bischoff, F. A.; Sauer, J.; Debnath, S.; Asmis, K. R.	Mixed Aluminium Iron Oxide-Clusters: Structures and Vibrations
P26	Jerabek, P.; Smits, O.; Peterson, K.; Pahl, E.; Schwerdtfeger, P.	Relativistic Effects in the Heaviest Element of the Periodic Table (and why it should not be called a Noble Gas)
P28	Atlam, F.; Awad, M.	Molecular Docking, Molecular Modeling, Vibrational and Biological Studies of Some New Heterocyclic Alpha-Aminophosphonates
P30	Bhat, H. R.; Rana, M. K.	Developing a DFT and TD-DFT Level of Theory for Designing BODIPY Based Anion Sensors and for their Mechanism Demonstration
P32	Friese, D.	Relativistic TD-DFT Calculations for Non-linear Optical Properties
P34	Liu, Y. Y.; Conduit, G.	Atomic Relaxation and Vibrational Modes in Quantum Monte Carlo
P36	Kruse, H.; Sponer, J.	Highly-Accurate Equilibrium Structure of the C_{2h} symmetric N1-to-O2 Hydrogen-bonded Uracil Dimer
P38	Bokarev, S. I.	Ultrafast Spin-flip Dynamics in Transition Metal Complexes Triggered by Soft X-ray Light
P40	Diezemann, G.; Kato, T.; Schäfer, K.; Jaschonek, S.	Molecular Simulation of the Remperature Dependence of the Mechanical Unfolding of a Supramolecular Complex
P42	Ahmed, A.; Kühn, O.	Ab Initio View on the Interaction of Glyphosate with Soil Components
P44	Wirz, L.; Dimitrova, M.; Reiter, K.; Fliegl, H.; Sundholm, D.	Magnetically Induced Electric Currents in Molecules with Unusual Topologies
P46	Melnikov, S.; Stein, M.	Solvation and Mobility of Carbon Dioxide in Aqueous Alkanolamines: a Molecular Dynamics Study

P48	Talotta, F.; Boggio-Pasqua, M.; Gonzalez, L.	SHARC Photodynamics of the TRANS-[RuCl(NO)Py ₄] ²⁺
P50	Frank, I.; Kraus, P.	The Tardy Dance of Molecular Orbitals
P52	Vasquez, L.; Dybala-Defratyka, A.	Isotope Effects by the Infinite Improbability Drive
P54	Schienbein, P.; Marx, D.	Electronic and Structural Properties along the Liquid-Vapor Coexistence Curve and in the Supercritical Phase of Water
P56	Börner, M.; Neugebauer, J.	Computational Studies on NHC-Ligands on Metal Surfaces
P58	Fan, C.; Springborg, M.	Inverse Design of Dye Sensitizers and QSPR Model of DSSC
P60	Krasowska, M.; Preda, AM.; Mehring, M.; Auer, A. A.	Heavy Main Group Element – π Interactions
P62	Giesen, S. M.; Hansmann, AK.; Berger, R.	Non-orthogonal Product Wave Function Approach for Electron Transfer Integrals
P64	Ruiz-Barragan, S.; Muñoz-Santiburcio, D.; Marx, D.	Improving the Description of the Graphene-water iIteraction: A New Electronic-structure-based Force Field
P66	Gaul, K.; Berger, R.	Automated Property Calculation for Fundamental Physics Tests with Molecules
P68	Zhou, M.; Springborg, M.; Kirtman, B.	Interplay Between Surface and Bulk Properties of Crystals
P70	Hansmann, AK.; Giesen, S. M.; Berger, R.	Molecular Energy Level Matching to Design Model Systems for Singlet Heterofission
P72	Hellström, M.; Hermansson, K.; Broqvist, P.; Behler, J.	Surface Phase Diagram Prediction from a Minimal Number of DFT Calculations

P74	Siemer, N.; Muñoz-Santiburcio, D.; Frenzel, J.; Marx, D.	Enhanced O_2 Activation Caused by Direct Contact to the Perimeter of Au/TiO ₂ Nanocatalyst
P76	Schwarzer, M. C.; Fujioka, A.; Ishii, T.; Ohmiya, H.; Mori, S.; Sawamura, M.	Non-covalent Interactions as a Guiding Principle in the Enantioselective Alkynylation of α -Ketoesters via Copper Catalysis
P78	Duran Caballero, L.; Roy, P. N.; Marx, D.	Microsolvation of the Water Molecule and Hydronium by Bosonic Helium
P80	Herbold, M.; Dickmanns, J.; Eckhoff, M.; Behler, J.	Development of a Neural Network Potential for Metal-Organic Frameworks
P82	Eckhoff, M.; Blöchl, P. E.; Behler, J.	A Neural Network Potential for Lithium Manganese Oxides
P84	Müller, P.; Bauer, M.; Kühne, T. D.	Experimental and Theoretical High Energy Resolution X-Ray Absorption Spectroscopy
P86	Küllmey, T.; Paulus, B.	Cu_2ZnSnS_4 Kesterite – Phase Stability under Pressure, Cd-Doping and Ag Analogues
P88	Huwig, K.; Grigoryan, V. G.; Springborg, M.	Global Optimization of Alkali Clusters: Application of a Modified Embedded Atom Method
P90	Yang, T.; Frenking, G.	20-Electron Octacarbonyl Anion Complexes $[TM(CO)_8]^-$ (TM = Sc, Y, La)
P92	Maity, S.; Bold, B.; Prajapati, J.; Elstner, M.; Kleinekathöfer, U.	QM/MM Dynamics to Study Excitation Energy Transfer in the FMO Light-Harvesting Complexes
P94	Dominikowska, J.; Palusiak, M.	Tuning Aromaticity of para-Substituted Benzene Derivatives
P96	Heller, E.; Joswig, JO.; Lorenz, T.; Seifert, G.	Two-Dimensional Phosphorus Carbide Polymorphs: Influence of Structural Motifs on the Band Gap
Р98	Leach, S.; Limberg, C.; Lokare, K. S.; Goikoetxea, I.; Sauer, J.; Baldauf, C.; Debnath, S.; Jorewitz, M.; Asmis, K.	Al and Mixed Al/Fe Oxide Gas-Phase Ionic Clusters: Theoretical Investigation for Spectroscopy Experiments
Potzel, O.; Taubmann, G.	Modeling the Pressure Dependence of the Hydrophobic Effect of Amyloids in Aqueous Solution	
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Schulz, A.; Jacob, C. R.	Description of Intermolecular Charge-Transfer with Subsystem Density-Functionals Theory	
Pieck, F.; Tonner, R.	Systematic Exploration of a Reaction Network by Density Functional Theory: The Growth of Gallium Phosphide on Semiconductor Surfaces	
Bedurke, F.; Klamroth, T.; Saalfrank, P.	Simulation of High Harmonic Generation Spectra for Molecular Isomers Using the Time-dependent Configuration Interaction Singles Method	
Williams, D.; Eisfeld, W.	Accurate Vibronic Quantum Dynamics of NO_3 Using a Diabatic Neural Network Potential	
Osthues, H.; Doltsinis, N. L.	Functionalization of MoS_2 with Light Switchable Azobenzene	
Ganta, P. B.; Ahmed, A.; Kühn, O.	Ab Initio Simulations of P-Compounds at Mineral Surfaces	
Bachmann, J.; Doltsinis, N.	An Extended Hamiltonian Approach to Adaptive QM/MM Simulations	
Uranga, J.; Dai, S.; Funk, LM.; Sautner, V.; Paulikat, M.; Schröder, B.; Mata, R. A.; Tittmann, K.	Low-barrier Hydrogen Bonds in Enzymes: a Static or Dynamic Concept?	
Khedkar, A.; Roemelt, M.	Automated Active Space Selection for DMRG-SCF based on 2nd Order Perturbation Theory	
Koch, T.; Doltsinis, N. L.	Modelling Charge Transport in Bulk Heterojunction Organic Solar Cells by Kinetic Monte Carlo Simulations	
Erhard, J.; Görling, A. G.	Kohn Sham Methods Based on the Adiabatic-connection Fluctuation-dissipationtheorem and Powerseriesapproximations for the Exchange-correlation Kernel	
Dempwolff, A. L.; Schneider, M. FM.; Dreuw, A.	Modeling Ionizations Using ADC	
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P126	Noetzel, J.; Imoto, S.; Forbert, H.; Marx, D.	Theoretical THz Spectroscopy of Aqueous Urea Solutions: From Ambient Conditions to High Hydrostatic Pressures
P128	Kaiser, D.; Sauer, S.; Erdmannsdörfer, J.; Michels, B.; Engels, B.	Materials Modelling, Multiscale Simulations and Global Optimization – New Features in the CAST Program Package
P130	Bensberg, M.; Neugebauer, J.	Cost Effective Reaction Energies for Organic Reactions from "Exact" WF-in-DFT Embedding
P132	Lemke, O.; Witek, J.; Riniker, S.; Keller, B. G.	Kinetic Models of the Cyclosporines A and E
P134	Dohmen, P.; Bold, B. M.; Höfener, S.; Kranz, J. J.; Kleinekathöfer, U.; Elstner, M.	Benchmark and Application of LC-DFTB on Light-Harvesting Complexes
P136	Mattsson, S.; Müller, C.; Paulus, B.	Ab initio Calculations of the Cohesive Energy of the low Temperature α Phase of Elemental F ₂
P138	Maag, D.; Kubař, T.; Elstner, M.; Gillet, N.	QM/MM Studies of Proton Coupled Electron Transfer in Ribonucleotide Reductase
P140	Liu, W.; Köhn, A.	A New Tool for Diabatization of Electronic Excitations
P142	Stoychev, G.; Auer, A. A.; Neese, F.	Calculation of NMR Chemical Shielding Tensors with Double-hybrid DFT. Development of DLPNO-MP2 Second Derivatives
P144	AlBaraghtheh, T.; Renziehausen, K.; Barth, I.	Quantum Hydrodynamics Approach for Calculating Non-zero Current Densities
P146	Scholz, L.; Neugebauer, J.	Investigating the Effect of Missing Inter-Subsystem Charge-Transfer Excitations in Subsystem TDDFT
P148	Bohle, F.; Grimme, S.	Influence of Dispersion Forces on Molecular Recognition in Solution
P150	Marefat Khah, A.; Reinholdt, P.; Kongsted, J.; Hättig, C.	The Impact of DNA-Confinement on The Photoisomerization of A Triazene: A PE-ADC(2) Study

P152	Dietrich, F.; Bernhard, D.; Strebert, P. H.; Fatima, M.; Schnell, M.; Suhm, M. A.; Gerhards, M.	The Role of Dispersion in the Structure of Diphenyl Ether Aggregates
P154	Taubmann, G.; Potzel, O.	Theoretical Investigation of the Solubilities of AgI and AgTcO $_4$
P156	Scheurer, M.; Herbst, M. F.; Reinholdt, P.; Olsen, J. M. H.; Dreuw, A.; Kongsted, J.	Polarizable Embedding Combined with the Algebraic Diagrammatic Construction: Investigating Electronic Excitations in Biomolecular Systems
P158	Brehm, M.; Thomas, M.	An Efficient Lossless Compression Algorithm for Trajectories of Atom Positions and Volumetric Data
P160	Schröder, B.	Variational Ro-vibrational Calculations for Linear Tetra Atomic Molecules Using Watsons Isomorphic Hamiltonian
P162	Ma, S.; Liu, W.; Rohnacher, V.; Hillebrandt, S.; Kühn, M.; Mankel, E.; Benneckendorf, F. S.; Jänsch, D.; Lovrincic, R.; Köhn, A.	Self-assembled Monolayers (SAMs) of Thiol-containing Organic Molecules Grafting on Gold Surface: a First-principles Study
P164	Laqua, H.; Kussmann, J.; Ochsenfeld, C.	Exchange-hole-normalization-DFT (xhn-DFT): A simple Model for Multi-reference Systems
P166	Schäfer, K.; Kolli, H. B.; Diezemann, G.; Gauss, J.; Milano, G.; Cascella, M.	Hybrid Particle-field Molecular Dynamics Simulations of a Charged Surfactant
P168	Dombrowski, D.; Weingart, O.	Influence of Vibrational Excitations on the Photoisomerization of Bacteriorhodopsin with OM3-MRCI/Amber
P170	Panek, J.; Jezierska, A.	Influence of Bridge Proton Position on the Interaction Energy of Homodimers of Molecules with Intramolecular Hydrogen Bonds
P172	Meitei, O. R.; Heßelmann, A.	A Practical Approach to Intramolecular Interactions via Molecular Fragmentation

P174	Weike, T.; Manthe, U.	Wave Packet Dynamics of Indistinguishable Particles with Contracted Orbitals
P176	Bauer, F.; Köhn, A.	Finding a Starting Guess for Transition Structure Optimisations: A Parallelised Auto-Adjusting Reaction Path Optimiser
P178	Boese, A. D.; Loboda, O. A.; Dolgonos, G. A.	Embedding QM:QM Methods for Molecular Crystals
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291 participants, in alphabetical order.

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Part II.

Book of Abstracts

6. Invited Talk Abstracts

Exploring Solvated Electrons by Explosive as well as Non-Explosive Experiments and Simulations

Pavel Jungwirth

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A dangerous but among school kids all-time favorite experiment demonstrating an explosive chemical reaction is throwing a piece of sodium in water. Every high school chemistry teacher knows that the explosion is due to release of electrons from the metal to water accompanied by formation of steam and molecular hydrogen, which can ignite during this exoergic process. The very same gases should, however, separate the reacting metal and water and thus quench the reaction. How come that the explosion occurs anyway? Using ultrafast cameras and ab initio as well as force field molecular dynamics simulations we have discovered a hitherto unknown primary mechanism of the explosive behavior of alkali metals in water. Namely, after migration of electrons from the metal to water the former acquires a huge positive charge. Thanks to mutual repulsion of these charges the metal undergoes a Coulomb explosion accompanied by ejection of metal spikes into water. This enables effective mixing of reactants, which is a necessary condition for the explosion. As an extra bonus, we also show how blue solvate electrons formed during this reaction can be observed with a naked eye despite their sub-millisecond lifetime in water and how they can be modeled using ab initio molecular dynamics simulations.

Mason, P.; Uhlig, F.; Vanek, V.; Buttersack, T.; Bauerecker, S.; Jungwirth, P.: Coulomb Explosion during the Early Stages of the Reaction of Alkali Metals with Water. Nature Chemistry, 7, 250 (2015).

Mason, P.; Buttersack, T.; Bauerecker, S.; Jungwirth, P.: A Non-Exploding Alkali Metal Drop on Water: From Blue Solvated Electrons to Bursting Molten Hydroxide. Angewandte Chemie, 55, 13019 (2016).



Chirality and Electron Transition Current Density in MolecularVibrations: VCD and ROA

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Vibrational optical activity (VOA) consists of two major subfields, infrared vibrational circular dichroism (VCD) and vibrational Raman optical activity (ROA) [1]. Both ROA and VCD were first measured experimentally in the early 1970s and while the theoretical basis of ROA can be described within the Born-Oppenheimer (BO), VCD cannot due to the vanishing of the electronic contribution to the magnetic-dipole transition moment within a non-degenerate electronic ground state (zero angular momentum within a single electronic state in the BO approximation) [2]. This problem was resolved conceptually with the complete adiabatic (CA) approximation by including the lowest-order correction to the BO approximation, without loss of factorization of the molecule wavefunction, which provides correlation between nuclear velocities and electron *current* density [3], whereas the BO approximate provides only correlations between nuclear positions and electron probability density. It was shown that using this nuclear velocity perturbation (NVP) formalism [4], electron current density and electron probability density obey the usual conservation of electron probability density at any point in the space of a molecule Subsequently, electron transition current density (TCD) was defined for vibrational [3,4]. transition which allowed visualization of the motion of electron probability density during vibrational transitions [5-7]. More recently, the NVP formalism has been applied for the first time to the calculation of vibrational circular dichroism (VCD) as an alternative to the established magnetic field perturbation (MFP) formalism available in programs from, for example, Gaussian 09 [8,9]. Examples of vibrational electron TCD will be provided and discussed, as well as directions for future applications of the TCD formalism.

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Competing interactions in ionic liquids: When cooperative hydrogen bonding overcomes Coulomb repulsion between ions of like charge

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"Unlike charges attract, but like charges repel". This conventional wisdom has been recently challenged for ionic liquids (ILs). Here we show that like-charged ions attract each other despite the powerful opposing electrostatic forces. In principle, cooperative hydrogen bonding between ions of like-charge can overcome the repulsive Coulomb interaction while pushing the limits of chemical bonding [1-7]. The key challenge of this solvation phenomenon is to establish design principles for the efficient formation of clusters of like-charged ions in ionic liquids. For that purpose, we combined weakly coordinating anions with polarizable cations, which are all equipped with hydroxyl groups for possible H-bonding. The formation of H-bonded cationic clusters can be controlled by the interaction strengths of the counterions and the delocalization of the positive charge on the cations [3,4]. Strongly interacting anions and localized charges on the cations and delocalized charge on the cations lead to the formation of H-

bonded cationic clusters up to cyclic tetramers. If we increase the distance between the hydroxyl groups and the positive charge centre on the cation we can further support the cationic cluster formation. These clusters are observed by bulk infrared (FT-IR) and cryogenic vibrational spectroscopy, and interpreted by density functional theory (DFT) calculations on neutral and ionic clusters [1-7]. The formation of cationic clusters is also reflected in the NMR proton chemical shifts and in the rotational correlation times of the OH groups. Additional molecular dynamics simulations (MD) provide information about the lifetimes of the hydrogen bonds in the cationic clusters compared to those in the typical ion pairs [7].



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Molecular understanding of organic-organic interfaces and mixtures

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We show how inclusion of mesoscale order resolves the controversy between experimental and theoretical results for the energy-level profile and alignment in a variety of photovoltaic systems, with direct experimental validation [1,2]. We explain how this order and interfacial roughness generate electrostatic forces that drive charge separation and prevent carrier trapping across a donor-acceptor interface [2].

Comparing several of small-molecule donor-fullerene combinations, we illustrate how tuning of molecular orientation and interfacial mixing leads to a trade-off between photovoltaic gap and charge-splitting and detrapping forces, with consequences for the design of efficient photovoltaic devices. By accounting for long-range mesoscale fields, we obtain the ionization energies in both crystalline [3] and mesoscopically amorphous systems with high accuracy [4].

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Water at interfaces:

structure and vibrational spectroscopy from ab initio simulations

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Water in contact with a solid surface may have properties substantially different from bulk ones, depending on the surface hydrophobicity/hydrophilicity, as well as on the surface charge. In this talk I will present a combined simulation and experimental approach aiming to understand structural and dynamical properties of water at the interface with calcium/fluorite over a wide range of pH conditions [1]. Density functional theory (DFT) -based molecular dynamics simulations can be used to compute phase-resolved Sum Frequency Generation (SFG) spectra [1,2] and to provide a molecular interpretation of the experimental spectra and a microscopic description of the interfaces. In a second part of the talk, I will present our approach to understand vibrational energy relaxation at interfaces using non-equilibrium molecular dynamics simulations and suitable descriptors based on projected vibrational density of states [3]. The data from the simulation permits to interpret experimental pump-probe SFG spectra. We find that the energy relaxation, mostly mediated by an OH-OH stretching coupling, is highly heterogenous and strongly depends on the environment, where a strong hydrogen bond network can transport energy with a timescale of 200 fs, whereas a weaker network can slow down the transport of a factor 2-3. Differences between interfacial and bulk water relaxation will be discussed.

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Electron transport in molecular junctions

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Molecular junctions, i.e. single molecules bound to metal or semiconductor electrodes, represent a versatile architecture to investigate molecules in a distinct nonequilibrium situation and, in a broader context, to study basic mechanisms of charge and energy transport at the nanoscale. The accurate theoretical treatment of electron transport in molecular junctions is challenging because it requires methods that are capable to describe the electronic structure and dynamics of molecules in a condensed phase environment out of equilibrium [1]. The combination of density functional theory (DFT) and nonequilibrium Green's function (NEGF) transport methods provides an established framework for cases, where electronic-vibrational interaction can be either neglected or treated perturbatively [2]. In this talk, methods are discussed, which allow the accurate treatment of electron transport in models with stronger electronic-vibrational interaction, including the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method [3,4] and the hierarchical quantum master equation (HQME) approach [5]. Moreover, the combination of the ML-MCTDH method with reduced density matrix theory is outlined [6]. The performance of the methods is discussed for typical models of molecular junctions, with a focus on vibrational nonequilibrium effects.

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Non-covalent interactions: from gas phase benchmarks to communication in enzymes

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With the availability of high resolution structural data, as well as through advances in timeresolved spectroscopy and computational methods, our understanding of enzymes has improved enormously over the last few years. Still, for the most part, we lack a global vision of the processes occurring in these complex systems. We might be able to draw up a mechanism for a chemical reaction occurring at an active site, but we then struggle finding the relation to large amplitude motions the enzyme effects, pH changes, specificities in the substrate or allosteric communication, only to name a few. How do all these factors come together? In this talk, the focus will be on the role of hydrogen bonds, one of the most important threads running through the canvas of enzymatic catalysis. Hydrogen bonds are able to establish long-lived channels of communication, which are often overseen due to our choice of simulation methods. Some recent studies carried out at our group include one of the record setters for catalysis, the human orotidine-5'-monophosphate decarboxylase, and ThDP-dependent[1] enzymes such as a transketolase and a pyruvate oxidase, whereby the cofactor is largely controlled through the surrounding hydrogen bond network. Our findings highlight the need for more accurate and encompassing descriptions (e.g., allowing for proton transfer events in the environment).

Focusing on the issue of accuracy, recent efforts for establishing highly accurate benchmark data for non-covalent interactions will also be detailed[2,3]. The latter build the basis for our studies in biomolecules, dealing with the question of competition between different forces (e.g., steric repulsion vs dispersion). Such balances are determining, for example, when dealing with chirality recognition.

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Vibrational Circular Dichroism Spectra From First-Principle Molecular Dynamics Simulations

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Vibrational circular dichroism (VCD) is the extension of circular dichroism (CD) spectroscopy to infrared wavelengths. The identification of absolute configurations with VCD is facilitated with respect to electronic CD because of the many absorption lines available. This makes VCD a sensitive analysis tool for the pharmaceutical industry. VCD can also probe efficiently interactions with the environment, such as hydrogen bonds with the solvent, and the conformation of flexible molecules. It is then desirable to push current theories to the study of VCD for fluxional molecules and condensed phases.

For this purpose, we have developed a method to compute VCD spectra from first-principle molecular dynamics simulations. The VCD spectrum is expressed as the Fourier transform of the time-correlation function of the dipole and magnetic moments. The electronic contribution to the magnetic moment however is identically zero in the Born-Oppenheimer approximation and is thus intrinsically non-adiabatic. We have developed a Nuclear Velocity Perturbation Theory (NVPT) based on the work from Nafie[1] for including perturbatively non-adiabatic effects. This allows for the evaluation of electronic currents induced by the nuclear motion, from which the magnetic moment is obtained in a proper gauge[2].

After describing the method and its implementation in the CPMD code, we will present some recent illustrations both in the liquid phase[2, 3] and in a crystal[4]. In particular we will discuss how coupled vibrational motions lead to chirality transfer from a chiral solute to an achiral solvent[2] and to VCD enhancement in L-alanin crystal, arising from the chiral arrangement of the L-alanine molecules[4]. Furthermore, we will discuss how NVPT can describe other non-adiabatic effects[5].

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Teaching new tricks to an old dog to quantify the degree of covalency of hydrogen bonding

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A new energy decomposition analysis method for periodic systems based on absolutely localized molecular orbitals is presented [1]. In combination with an accurate and efficient technique to compute nuclear quantum effects and the previously developed second generation Car-Parrinello molecular dynamics approach [2, 3], this not only allows for quantum molecular dynamics simulations on previously inaccessible length and time scales, but also provide unprecedented insights into the nature of hydrogen bonding between water molecules. The effectiveness of this new combined approach is demonstrated on liquid water, ice and the water/air interface [4]. Our simulations reveal that although a water molecule forms, on average, two strong donor and two strong acceptor bonds, there is a significant asymmetry in the energy of these contacts [5]. We demonstrate that this asymmetry is a result of small instantaneous distortions of hydrogen bonds and show that the distinct features of vibrational and X-ray absorption spectra originate from molecules with high instantaneous asymmetry [6, 7]. Moreover, we found a striking correlation between the covalency of a hydrogen bond and the anisotropy of the proton magnetic shielding tensor, which enables to experimentally determine the strength and charge transfer of hydrogen bonding by NMR [8].

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Molecular simulations of lipid membrane sensing

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Living cells need to exert tight control over their lipid membranes to maintain their internal structure, to guard their outside boundary, to establish potential and concentration gradients as their energy source, and to transmit signals between their compartments and to the outside. As a consequence, elaborate machineries have evolved that allow cells to sense and regulate both shapes and physical characteristics of their lipid membranes. In my talk I will give an overview of the physics and chemistry used by these machineries, as identified by molecular dynamics simulations combined with experiments. Remarkably, a range of distinct non-covalent interactions play critical roles in membrane sensing in order to probe the packing, order, charge, and specific chemistries of the membranes.

Solvent effects in core- and valence-level photoionization spectroscopy

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Understanding how solvent affects the electronic properties of solutes is of paramount importance for chemistry. Particularly important are local solvent structure around solvated molecules and the changes in the shapes and energies of solute's orbitals induced by the interactions with the solvent. Experimentally these properties can be probed by various types of photoelectron spectroscopies combined with the theoretical modeling. This lecture will outline challenges for theoretical modeling of bulk photoionization spectra, describe recent progress in first-principle modeling of valence and core-level spectra, and present illustrative results. The examples include core and valence spectra of aminoacids and photoelectron angular distributions of bulk water.

7. Contributed Talk Abstracts
QM/QM models of a molecular mechanism controlling photoprotective quenching in higher plants

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Plants need to safely quench surplus excitation energy from their photosynthetic antennae under excess light conditions to prevent photochemical damage, a process known as non-photochemical quenching (NPQ). The mechanisms proposed for NPQ in the major light harvesting complex II (LHCII) so far are based on the involvement of quenching compounds such as carotenoids although clear spectroscopic evidence supporting such mechanisms is lacking¹.

Based on earlier experiments ²⁻⁴ we further characterized several far-red emitting chlorophyll states that are active under different crystallization or aggregation conditions, while not present in the unquenched trimeric LHCII. By combining the results of ultrafast fluorescence experiments with long-range corrected density functional theory calculations in an ONIOM scheme, we were able to find that these states originate from a triad of chloropyhll molecules, which are extremely sensitive to the local charge distribution. Nearby amino acids were found to act as switches, static charges and sensors.

We thus propose an NPQ mechanism based on the reprotonation of an amino acid pair (Glu175/Lys179) located at the surface of the major light harvesting complex II (LHCII). This pair is conserved throughout the different varieties of LHCII variants and is located at the threshold between membrane and solvent. We propose its role to be the "gatekeeper" for another reprotonation event which leads to the formation of Chl-Chl charge transfer (CT) states. These CT states provide the dissipative channel to remove excess energy form the system, without the need for any further supporting compounds. We suggest that the CT state formation is controlled via interaction with the amino acid pair.

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Improved partitioning of biomolecules for quantum-chemical embedding calculations based on graph theory

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Quantum-chemical subsystem methods [1] allow for the efficient calculations of local molecular properties, such as local excitation energies in biomolecular systems. To this end, the system is partitioned into a subsystem of interest (e.g., the chromophore) and its environment. This environment is usually further partitioned into smaller fragments [2]. For protein environments, a partitioning into fragments containing a fixed number of amino acids has so far been employed [3].

Here, we employ methods from graph theory to determine the partitioning of protein environments for quantum-chemical embedding calculations of local molecular properties. The main challenge is to map the protein structure onto a graph in which the nodes are the amino acid residues connected by edges. Depending on the strength of interaction and distance to the subsystem of interest, weights are assigned to the edges. These have to be chosen in a way that they estimate the error in the property of interest that is expected when assigning its two nodes to different subsystems. To obtain these weights, we employed DFT calculations for all pairs of amino acids in small proteins. Based on these graphs, we use heuristics and cut-offs for larger protein test cases where the direct calculation becomes computationally infeasible [4].

We then apply graph partitioning algorithms for partitioning the protein graphs into blocks with the low cut weights, i.e., the partitioning for which the estimated error in the local molecular property is low for a given number of fragments. Established graph partitioning tools had to be modified to be applied directly to such protein graphs, as some additional constraints had to be introduced due to chemical idiosyncracies [5].

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Beyond Rosenfeld Equation: Computation of Vibrational Circular Dichroism Spectra for Anisotropic Solutions

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The fundamental theory behind absorption of circularly polarised light by enantiomeric pairs of chiral molecules can be described by the Rosenfeld equation [1] for randomly oriented samples. It describes the difference in absorption belonging to a vibrational or electronic transition between two states. Despite the simple form of the Rosenfeld equation, its evaluation in the infrared regime remained challenging as the contribution from the magnetic dipole operator is zero within the Born-Oppenheimer (BO) approximation for non-degenerated singlet electronic ground states [2]. In order to resolve this issue, "beyond BO" theories were developed [3, 4, 5], from which Stephen's magnetic field perturbation (MFP) approach offers a computationally easily accessible form [4]. It allows to evaluate the magnetic dipole transition moments of isotropic vibrational circular dichroism (VCD) efficiently, depending solely on an accurate description of the electronic ground state. Similar to Rosenfeld, Go derived an expression of the rotational strength valid for a cylindrical symmetric solution [6]. Due to the mathematical similarity, we show that Stephen's MFP theory can be adjusted to calculate rotational strengths valid for Go's equation. Our calculations found that VCD spectra of anisotropic solutions deviate substantially from isotropic solutions. Moreover, since spherical symmetry is broken, Go's equation offers additional structural information, which potentially provides a basis for future developments, in order to improve the reliability of absolute stereochemistry assignment from VCD experiments.

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On the Theoretical Optimization of Properties

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During the last few decades, theoretical calculations have become of increasing importance in providing supporting and complementary information to what is provided by experiment. On the one side, such studies can help in the interpretation of experimental results and, on the other side, through such calculations a first screening of systems can be carried through, ultimately allowing for reducing the synthetic work in the lab. In all those cases, the conventional approach is to start with a realistic structure for the system of interest whose stoichiometry is known, subsequently let the system relax to a close structure of a local total-energy minimum, and finally for this calculate the properties of interest.

The situation is different when essentially nothing is known about the structure of the system of interest. This is, e.g., the case for clusters and nanoparticles. For such systems, specialized theoretical methods that aim at identifying the global total-energy minima have to be applied. Another challenge is to identify molecular systems with optimal properties without specifying the stoichiometry.

In the present contribution we shall at first demonstrate how methods based on genetic algorithms can be used in optimizing the structure of nanoparticles. Subsequently, related methods will be used in identifying molecular systems with optimal properties, whereby at first,

as a playground system, mixed Ge-Si clusters with optimal properties in solar-energy harvesting shall be identified. Subsequently, modified benzene molecules shall be treated. The purpose of this method, PooMa, is to provide useful information for experiments about interesting systems with predefined properties. It is based on many approximations and is not aimed at providing exact information on any detail. PooMa is developed as a simple, efficient method that does not rely on heavy computations or results from, e.g., highthroughput studies.



PooMa:

M. Springborg, S. Kohaut, Y. Dong, and K. Huwig: *Mixed Si-Ge clusters, solar-energy harvesting, and inverse-design methods,* Comp. Theo. Chem. **1107** (2017) 14-22.

K. Huwig, C. Fan, and M. Springborg: *From properties to materials: an efficient and simple approach*. J. Chem. Phys. **147** (2017) 234105.

Hybrid Exchange Density Functionals within the Local Range Separation Scheme

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Due to a combination of efficiency and accuracy, density functional theory (DFT) is the most popular method to characterize the electronic structure of molecules and solids. The quality of the result depends strongly on the underlying density functional approximation for exchange and correlation interactions.

In range separated hybrid functionals, the exchange interaction is partitioned into a short- and a long-range part. For molecules, charge-transfer excitations in particular can be predicted with remarkable accuracy by using exact exchange at long range and thus correcting the asymptotic decay of the potential. The range separation parameter that determines the average distance at which the functional switches from short to long range is not defined uniquely and often fitted to experimental data. Alternatively, it can be tuned for a given system by imposing Koopman's theorem. Such optimally tuned range separated functionals yield significantly improved electronic spectra and excitation energies [1]. They are, however, of limited use for binding energies or potential energy surfaces due to a lack of size consistency[2] and, more generally, for very heterogeneous systems, in which the optimal range-separation parameter varies considerably in the different regions.

As a possible remedy, the range separation parameter can be replaced by a function in Cartesian space, giving rise to the local range separation scheme. Based on this previously proposed concept[3], we present the first self-consistent implementation of exchange functionals with local range separation. Using a semi-empirical approach, four parameters in the range separation function are adjusted to small training sets. For the short-range exchange, two different functionals, namely Slater and PBE, are considered and paired with their respective counterpart for correlation. The resulting functionals are subsequently assessed for binding energies and properties associated with the electronic eigenvalue spectra.

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Global geometry optimization of molecular assemblies on surfaces

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After 20 years of successfully applying Evolutionary Algorithms to the global optimization of cluster structures *in vacuo*, we have recently extended the capabilities of our versatile global optimization program package OGOLEM [1] to clusters on surfaces.

With this setup, we have explored homogeneous and heterogeneous atomic clusters on surfaces [2], using strain as diagnostic criterion and rationalizing a broad spectrum of structures, ranging from single-layer ad-clusters via various multilayer forms all the way to gas-phase-like structures almost not influenced by the surface attachment.

Ongoing work focuses on molecular clusters on surfaces, for example on derivatives of the triaza-triangulenium "TATA platform" system that has been frequently used both as molecular tether and as molecular spacer. With limited computational effort [3], we could explain key experimental observations of TATA monolayer formation [4].



Figure 1: Global optimization of 12 TATA-platform molecules with octyl spacers, on Au(111).

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Proton transfer mechanisms in basic solutions and at the oxide/water interface revealed by neural networks

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Proton transfer (PT) reactions play an important role in many fields of chemistry, for example during homogeneous and heterogeneous catalysis. Here, we develop high-dimensional neural network potentials [1] (NNPs) to elucidate the predominant PT mechanisms for water dissociation at the ZnO/liquid-water interface [2] and in NaOH(aq) solutions of different concentrations [3-5]. NNPs are computationally inexpensive and can accurately reproduce ab initio potential energy surfaces.

NNP-based molecular dynamics simulations reveal that PT reactions are coupled to fluctuations in the hydrogen-bonding environment around the proton donors and acceptors. We find that there is an unexpected similarity for the most predominant PT mechanisms at the ZnO/liquid-water interface and in NaOH(aq) solutions of high concentrations, which we explain by the influence that the cations (Zn^{2+} and Na^+) have on the hydrogen-bonding environment around the dissociating water molecules.



Different systems but similar proton transfer mechanisms. Left: The ZnO/liquid-water interface, and right: 15 mol/L NaOH(aq).

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Ab Initio Anisotropic Displacement Parameters of Molecular Crystals

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For decades already, anisotropic displacement parameters (ADPs) usually depicted as ORTEP plots have been used in crystallography and related fields to describe and quantify thermal atomic motion. Within the very recent years, these ADPs have become predictable by *ab initio* calculations.

This contribution will show how theoretical, yet reliable ADPs for molecular crystals with very different non-covalent interactions can be calculated with a combination of (quasi-)harmonic lattice-dynamics and dispersion-corrected density-functional theory [1,2,3,4]. Exemplarily, Figure 1 provides the excellent agreement between calculated and experimental ADPs of $Cr(CO)_6$:



Figure 1. Comparison of experimental and computed ADPs of Cr(CO)₆. This figure is taken from reference [4]. The article is licensed under a Creative Commons Attribution 3.0 Unported License (https://creativecommons.org/licenses/by/3.0/).

Furthermore, the usefulness of the calculated ADPs for complementing diffraction experiments facing problems due to an unfortunate data-to-parameter relationship will be demonstrated using several examples.

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Strain and non-covalent interactions as driving forces for surface reactivity

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Silicon is one of the most important elements in material science and its low-index surfaces are widely used substrates in technological applications. Increasing research efforts are recently made toward functionalizing the surface with organic and inorganic adsorbates. Intriguingly, the constraints imposed on the silicon atoms as being part of a solid surface create arrangements that are hard to achieve in molecular chemistry and lead to surprising reactivity. One prominent example is the buckled dimer at the reconstructed Si(001) surface (Fig. 1) which barely has molecular analogues.[1] Notably, saturated subsurface atoms (Si_{sub}) can also play a key role in the observed surface chemistry. We explored the impact of this unusual arrangement and the resulting strain on the reactivity toward adsorbates. Different levels of strain in the adsorbates may also influence the adsorption dynamics and reactivity significantly. Beside strain, non-covalent interactions can be the determining factors in the quest to build up organic-inorganic hybrid interfaces.[2] The observed reactivity patterns will be explained with electronic structure analysis including our recently developed energy decomposition analysis for extended systems (pEDA).[3]



Figure 1. (a) Si(001) surface reconstruction process. Dots indicate unpaired electrons. (b) The most stable reconstruction Si(001)c(4×2). (c) Crystal orbitals of a Si(001) slab at the Γ point.

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Coupled-Cluster Treatment of Molecular Strong-Field Ionization

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Molecules exposed to electric or electromagnetic fields of a strength comparable to the internal molecular forces undergo ionization, possibly accompanied by dissociation [1, 2]. This process underlies numerous phenomena involving strong fields such as molecular high-harmonic generation, laser-induced electron diffraction, and Coulomb explosion. Therefore, the quantitative modeling of molecular strong-field ionization rates is of immediate interest for the interpretation of all experiments in which strong fields are applied.

Within Hermitian quantum mechanics, strong-field ionization rates can only be determined from the time-dependent Schrödinger equation. On the contrary, a time-independent treatment is possible using complex-variable (CV) techniques from non-Hermitian quantum mechanics, where the ionization rate can be evaluated from discrete complex eigenvalues of the molecular Hamiltonian [3].

This contribution will discuss differences between autoionization and strong-field ionization and how this demands different CV techniques and electronic-structure methods [4, 5]. An implementation for the computation of molecular strong-field ionization rates at coupled-cluster levels of theory in a basis set of atom-centered Gaussian functions with a complex-scaled exponent will be presented [5, 6].

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

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Analytical gradient for a pair natural orbital-based local MP2 method, and for faster double-hybrid density functional geometry optimizations

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Local correlation methods based on pair natural orbitals (PNOs)[1, 2] have gained an increasing popularity over the past decade: for example, coupled cluster calculations can be performed for systems containing several hundred atoms, while errors in relative energies introduced by the approximations are within chemical accuracy.[3] The usefulness of PNO-based methodology for single-point energies of molecular systems has been established in a large number of application studies; however, optimizing geometries and calculating many properties requires the implementation of derivatives. Whereas analytic gradients had been developed for purely domain-based methods in the past,[4] somewhat less effort has been dedicated to methods constructed with PNOs.

We present the analytical gradient for the domain-based local pair natural orbital MP2 method (DLPNO-MP2).[5] It builds upon a complete Lagrangian formalism for the DLPNO-MP2 energy functional that includes the relaxation of PNOs, leading to a precise gradient of the energy without neglecting any contributions.[6] Double-hybrid density functionals and spin-component scaling are supported by the implementation, allowing accurate geometry optimizations to be performed for large systems well beyond the range of routine RI-MP2 calculations. The computational cost for a single-point energy and gradient calculation with DLPNO-MP2 is typically about 3-5 times higher than for Hartree-Fock or hybrid DFT functionals with the efficient RI-J and chain-of-spheres exchange approximations. Calculations become more efficient than RI-MP2 for systems containing at least 50-60 atoms (including hydrogens), and geometry optimizations converge for "floppy" systems which commonly occur when studying noncovalent interactions.

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On the Importance of Choosing an Adequate Active Space for Large-Scale Multireference Calculations

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The choice of the active space is essential for all quantum chemical calculations that employ multireference methods. If it is chosen too small, important aspects of the chemical problem at hand might be neglected and not be correctly described while a too large active space causes severe convergence problems during the orbital optimization and large unnecessary computational costs. For small systems like mononuclear transition metal complexes the selection of the active space can be done on the basis of "chemical intuition". While this procedure has been proven successful in many instances it will meet its limits for large and complex systems that are now accessible with modern approximate methods such as the density matrix renormalization group (DMRG) or the full-CI quantum Monte-Carlo (FCIQMC). The importance of the active space selection for qualitatively and quantitatively correct results will be highlighted by a theoretical study of the exchange coupling interaction in a biomimetic mixed valence manganese complex using the DMRG together with a perturbative description of dynamic electron correlation.[1] In particular, the influence of different groups of active orbitals on the obtained results along with some critical technical issues will be discussed. Furthermore, an automated selection scheme for the active space based on second order perturbation theory will be presented. Within this scheme the active orbitals are chosen according to their occupation number which is a well-defined and well established measure.[2]

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Closed-shell paramagnetism revisited: A low-field effect due to a strong-field three-state avoided crossing

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Most closed-shell molecules respond diamagnetically in a magnetic field, raising the total energy. Some closed-shell molecules, however, are paramagnetic, an effect that should not occur in a diabatic picture but is observed both in experiment and quantum-chemical calculations. Based on a two-state model, in Ref. 1, it was reasoned that a coupling with a low-lying excited state should be responsible for the paramagnetic response of the ground state. In the meantime, finite-field calculations for ground and excited states have become feasible within the framework of Coupled-Cluster (CC)[2] and Equation-Of-Motion (EOM) CC[3] theory. In this talk, we study the occurrence of closed-shell paramagnetism through finite-field CC and EOM-CC calculations for BH and CH⁺ in varying orientations with respect to the magnetic field. In the parallel orientation, three states cross at magnetic field of ~0.25 B₀ which corresponds to about 59000 Tesla (see Fig. 1, left). Rotating the molecule out of alignment breaks the symmetry, thereby inducing a three-state-avoided crossing which eventually leads to the paramagnetic response (see Fig. 1, middle and right). The rationalization is confirmed via an angle-dependent three-state model, reproducing the observed behavior.



Fig. 1: The ${}^{1}\Sigma$ ground state and ${}^{1}\Pi$ and ${}^{1}\Delta$ excited states of BH in different orientations (0°, 5°, and 50°) as a function of the magnetic field.

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Conceptual Framework of Molecular Electronics

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Non-covalent interactions are important across a range of organic electronic materials, from molecular semiconductors (e.g., the crystalline organic semiconductors) to molecular junctions (such as dimer bridges in scanning tunnelling microscope experiments). These intermolecular interactions depend on the nature of molecular cores and define not only the stability of their non-covalent assembly, but also its charge transport properties.[1]



In the present contribution, we draw a parallel between the transport in the nanogap between metallic electrodes and charge carrier mobility in the bulk of an organic semiconductor.[2] We show that, within the model approximations, the same systems are consistently among the best and the worst performers, with similar principles guiding their performance in the two types of materials. More generally, we establish a conceptual framework for various non-covalent molecular electronic architectures that connects intrinsic properties of molecular cores with the properties of their non-covalent assemblies (see Figure). These results demonstrate the unifying footprint of the fundamental electronic structure of molecular cores on the diverse charge transport properties and offer the design strategies for more conductive organic electronic devices.

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Hierarchical Method to Determine the Entropy of Molecular Systems

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A defining feature of systems with numerous non-bonded interactions is the close spacing and significant degeneracy of their energy levels. This leads to a system having an entropy on par with its energy, and its resulting stability being a delicate balance between entropy and energy. However, no such balance exists in the scientific effort put into evaluating energy and entropy. The substantial effort in evaluating energy, whether with electronic-structure methods or force fields, is not matched by equivalent efforts to evaluate entropy. Efforts to quantify the flexibility of molecular systems fall far short of capturing the complete flexibility, as quantified by entropy. This makes doubly pressing the need for better entropy methods. Building on previous work for liquids [1,2,3] and isolated, flexible molecules [4], we present new theory to calculate the entropy directly from a molecular dynamics simulation for the significant and rarely explored case of liquids of flexible molecules [5]. The entropy is evaluated at multiple length scales, with each level split into vibrational and topographical terms, the former representing the size of an energy well and the latter the number of energy wells. The vibrational term is derived from covariance matrices of forces and torques. The topographical entropic term encompassing conformations and orientations uses the probability distributions of dihedrals and molecular contacts defined using the parameter-free RAD algorithm [6]. The theory is tested on a range of liquids and is found to give reasonable agreement with experiment as well as an insightful decomposition of entropy over all degrees of freedom.

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Twist and shine: Organic TADF emerges from the interplay of non-covalent interactions, triplet-exciton delocalization, and post Franck-Condon effects.

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Thermally-activated delayed fluorescence (TADF) has recently gained much attention as it enables a harvesting of triplet excitons with purely organic OLED emitters, thereby increasing the theoretical maximum quantum yield from 25% to 100% without the need for expensive and toxic heavy metals. Computational studies of the phenomenon are hampered by a number of methodological issues related to the description of charge-transfer (CT) states in dielectric environments. As a result, modeling TADF with prominent approaches like TD-DFT/LR-PCM provides rates many orders of magnitude too low compared to experiments, which has so far impeded the theoretical understanding of the phenomenon.

In this contribution, I demonstrate a quantitative calculation of TADF rates for three typical emitters using a hierachy of ab-initio and DFT-based methods which rigorously include dielectric polarization. It is shown that (i) the character of lowest excited singlet and triplet states changes and becomes dominated by CT character already in apolar environments, (ii) shallow plateaus in the excited-state PES of the donor-acceptor twisting coordinate cause the transition properties to be governed by thermal fluctuations rather than the minimum-energy geometries, and (iii) the triplet CT state exhibits an exchange-driven delocalization (c.f. Fig. 1) that enables fast equilibration between the singlet and triplet manifolds *via* (reverse) inter-system crossing (ISC). Based on these insights, a simple mechanism is suggested that involves only the lowest lying singlet and triplet excited states and provides good agreement with experimental data.



Figure 1: Adiabatic energies and electron-hole plots of the excited states of a typical emitter in gas phase (left) and equibrated in a dielectric environment (right).

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Simple Models for Mechanochemistry

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An external mechanical or electrical force can change a chemical reactivity. We explain this for simple models:

- for triatomic ABC-molecules,
- for a simplified hairpin, and

- for a minimal model of a biomotor [1]. The main tool to understand the external force is the theory of Newton trajectories (NT) [2] - [5].

The curves are defined by the property that along an NT the gradient of the potential energy surface (PES) does not change its direction. Under the force, the stationary points of the PES change: they move along an NT.



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Applying Quantum Chemistry to Reactivity in the Condensed Phase

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Increasing computational power together with increasing accuracy of standard quantum chemical methods are the main drivers for their use of in the chemical industry [1]. In this presentation, an overview of routinely applied methods in industry is given. In detail, we discuss how reactivity in homogeneous catalysis is modelled using continuum solvation. Reactions involving chemisorbed molecules on surfaces in aqueous solution challenge the workflow based on solvation models and alternative approaches for heterogeneous systems are presented and discussed.

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Digital Finance at Deutsche Bahn AG

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Theorists have been engaged in finance for years to model derivative products or to quantify financial risks. Nowadays, the phenomenon of digitization is affecting every industry and there is a growing demand of digital and theoretical skills that are needed for jobs at every level. In this context, we present current use cases at Deutsche Bahn AG ranging from derivative modelling challenges to text mining and robotics.

Neural networks trained on ab-initio data for executing surface hopping molecular dynamics

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Excited state ab-initio molecular dynamics (AIMD) is a powerful tool to investigate photoinduced processes in molecules, but it is seriously limited by the cost of the underlying onthe-fly quantum chemical calculations, hampering its application for long timescales. In this work, we face this bottleneck by combining conventional AIMD with machine-learning algorithms. In detail, we employ the surface hopping molecular dynamics program suite SHARC (Surface Hopping including ARbitrary Couplings) [1, 2], in which the demanding quantum chemistry calculations have been replaced with predictions made by multi-layer feed-forward neural networks (NNs), providing remarkable computational efficiency. Reference data points for training of NNs are generated with quantum chemistry programs via grid sampling and an adaptive sampling scheme [3]. To guarantee that NNs predict properties correctly, we apply an active learning approach similar to reference [4] by using two NNs and comparing their outputs on-the-fly. Results are shown for an analytical model and a test molecule with 12 degrees of freedom.



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Structural Basis of the Red/Green Spectral Tuning in the Cyanobacteriochrome Slr1393

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Cyanobacteriochromes (CBCRs) are promising candidates for use in biotechnological applications, owing to their photochromism, compactness and spectral diversity. In case of the CBCR Slr1393, one isomer absorbs red light (P_R) and the other one green (P_G) (Fig. 1 B) [1]. The two forms can be interconverted into each other by light illumination. Slr1393 binds phycocyanobilin (PCB) as chromophore and the crystal structures of both forms have been obtained recently. Comparing PCB from both structures shows that one double bond isomerization occurs during the photoconversion (Fig. 1 A). In this contribution, results of hybrid quantum mechanics/molecular mechanics (QM/MM) calculations for the P_R and P_G forms of Slr1393 will be presented [2].



Figure 1: (A) Reaction scheme of PCB photoisomerization, the wavelengths refer to the experimental absorption maxima; (B) Simulated absorption for the P_R (red) and P_G (green) forms of PCB based on 100 structures for each form from QM/MM MD and computed with RI-ADC(2)/cc-pVDZ.

Our QM/MM studies started from the crystal structures. First, the structures were optimized in several stages, followed by classical molecular dynamics (MD) for thermalization and backbone relaxation. During these steps, it was checked that the non-covalent interactions of PCB with the protein remained intact. The snapshots for excited state calculations were then generated via QM/MM MD. The final spectrum is an average of the spectra from the different conformations of each form and the results are complemented with wave function analysis.

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Non-zero electron current densities for the vibrating hydrogen molecular ion in a single electronic Born-Oppenheimer ground state

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Using the well-known formula for the electron current density, one can calculate the electron current density from the given wave function. However, for vibrating molecules in a single electronic non-degenerate ground state, the electron current density is untruly zero when the Born-Oppenheimer (BO) approximation is applied. The well-known continuity equation does not help much if one wants to calculate two- or three-dimensional current densities. Thus, we find out that using the quantum hydrodynamics approach one is able to obtain non-zero electron current densities for vibrating molecules (for example H_2^+) or even chemical reactions in a single electronic non-degenerate BO ground state. We have derived the many-particle Ehrenfest equation of motion [1] containing the time derivative of the mass current density. We checked it successfully for some simple test systems including *s*-wave functions of a hydrogen atom [2] and Gaussian wave packets in a two-dimensional harmonic potential. We also show first results for non-zero electron current densities for the vibrating H_2^+ molecule in a single electronic ground state.

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The Mechanism of Overhauser Dynamic Nuclear Polarization in Insulating Solids

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The last decade has seen revolutionary developments in the methods for hyperpolarizing nuclear spins in NMR spectroscopy. The generality of these methods, in particular those based on dynamic nuclear polarization (DNP), has lead to a wide range of exciting applications that were simply unreachable before the advent of these techniques. In the heart of DNP is always a polarization transfer mechanism that endows nuclei with much larger electronic spin polarization. One possible mechanism for this polarization transfer, the Overhauser effect (OE-DNP), is traditionally known to be operative only in liquids and conducting solids. Very recently, surprisingly strong OE-DNP in insulating solids has been reported, which was shown to offer several appealing features that would make it the method of choice in many applications, but a rational optimization of the technique requires an understanding of the underlying molecular mechanism. Here we offer an explanation for this perplexing finding that elucidates the underlying molecular stochastic motion, provides cross-relaxation rates, explains the observed sign of the NMR enhancement, and estimates the role of nuclear spin diffusion..[1] This has been possible by combining the *ab initio* calculation of magnetic resonance parameters, with the explicit sampling of time-dependent fluctuations that is afforded by molecular dynamics simulations, and then by performing spin dynamics simulations based on numerical solution of the Liouville-von Neumann equation of motion for a model spin system. The presented theoretical description opens the door for rational design of novel polarizing agents for OE-DNP in insulating solids, and in a more general perspective, provides a pathway to the calculation magnetic relaxation rates and line shapes.

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DFT–D4: An accurate and generally applicable tight-binding based dispersion correction for density functional theory

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The finalized version of the DFT-D4 model is presented for the efficient computation of London dispersion interactions with DFT. Dynamic dipole polarizabilities have been calculated with TD-PBE38/daug-def2-QZVP to generate atomic reference polarizabilities for elements up to radon (Z=86) [1]. In DFT-D4, all atomic reference polarizabilities are scaled according to Mulliken partial charges q which are obtained by the recently developed tight-binding method GFN2-xTB. For the scaling of the atomic reference polarizabilities a special charge-function was designed containing one global parameter to get a smooth scaling behavior. Additionally, semi-empirically determined chemical hardnesses [2] control the slope of the function. The charge-scaled dipole polarizabilities are Gaussian interpolated according to an empirically generated fractional coordination number to obtain the fully weighted dynamic polarizabilities $\alpha(i\omega)$ for all atoms which are then numerically integrated via the Casimir–Polder scheme to obtain charge- and geometry-dependent dipole-dipole dispersion coefficients. The twobody energy expression has the usual sum over pair interactions form for dipole-dipole and dipole-quadrupole interactions. Based on this expression, a self-consistent dispersion potential has been developed and implemented into the GFN2-xTB Hamiltonian to circumvent a costly coupled-perturbed SCF procedure when calculating analytical gradients. Furthermore, dynamic polarizabilities $\alpha(i\omega)$ are used within an RPA-like expression to capture many-body interactions beyond the two-body terms. Various benchmark sets show a significant improvement over DFT–D3-ATM(BJ) results by applying the DFT–D4 correction.



- Figure 1: Left: host-guest complexes with diverse interaction motifs like anions, highly charged complexes (-1 up to +4) as well as large systems up to 200 atoms. **Right:** thermochemical benchmark set of realistic closed-shell metal organic reactions. The reference uncertainty of ≈ 2 kcal mol⁻¹ is shown in both plots in gray.
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Statistical Analysis of Semiclassical Dispersion Corrections

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Semiclassical dispersion corrections developed by Grimme and coworkers have become indispensable in applications of density functional theory. We present an in-depth assessment of the fit parameters present in semiclassical (D3-type) dispersion corrections by means of a statistically rigorous analysis. We find that the choice of the cost function generally has a small effect on the empirical parameters of D3-type dispersion corrections. However, the weighting scheme in the cost function can significantly affect the reliability of predictions. In order to obtain unbiased (data-independent) uncertainty estimates for both the empirical fit parameters and the corresponding predictions, we carried out a nonparametric bootstrap analysis. The mean prediction uncertainty obtained by bootstrapping is not much larger than previously reported error measures. On the basis of a jackknife analysis, we find that the original reference set is slightly skewed, but our results also suggest that this hardly affects the prediction of dispersion energies. A rigorous analysis of error accumulation arising from different parameterizations reveals that error cancellation does not necessarily occur, leading to a monotonically increasing deviation in the dispersion energy with increasing molecule size. We discuss this issue in detail at the prominent example of the C₆₀ "buckycatcher". We find deviations between individual parameterizations of several tens of kcal/mol in some cases. Hence, in combination with any calculation of dispersion energies, we recommend to always determine the associated uncertainties for which we will provide a software tool [1].

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Can you do more? - Yes! Quantum dot inter-Coulombic decay with *three* electrons

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In recent years the well-known inter-Coulombic decay process [1, 2] was by an electron dynamics treatment predicted to happen in paired and singly-charged quantum dots (QDs) [3, 4, 5]. Both QDs are distant enough from each other that their electrons are solely coupled by Coulomb interaction. QD-ICD then occurs when an electron in an excited state transfers its energy to the other dot's electron ionizing it.

ICD for atoms and molecules has among others been analyzed in the framework of a virtual photon transfer process and described by an asymptotic dipole-dipole coupling formalism [6]. There it was stated that the rate for ICD linearly increases with the number of neighbors, as was confirmed by several of the following ICD studies [2].

In this work we calculate for the first time QD-ICD in a three-electron three-quantum dot array and analyze its electron dynamics and rate dependence with respect to the number of newly available decay channels.

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Photodynamics and spectroscopy of halogens embedded in rare gas solids Quantum dynamical description of the I₂ : Kr system

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Diatomic halogen molecules embedded in rare gas crystals provide prototypes for the investigation of condensed phase chemical dynamics.[1,2] Nonlinear spectroscopy experiments performed on these systems reveal strong guest-host interactions and manifestations of quantum effects such as entanglement between system and environment, non-local correlations, and the transition to classicality through decoherence.[3,4]

Such pronounced quantum behaviour is also ideally suited for testing novel computational approaches to describe the dynamics of open quantum systems.[5] In this contribution, we study cluster models of I₂ in a fcc Kr crystal, by comparing two wave packet propagation methods: (i) the numerically exact multiconfigurational time-dependent Hartree (MCTDH) approach,[6] and (ii) the G-MCTDH variant,[7] in which the rare gas cage coordinates are treated with Gaussian wave packets. Due to anharmonicities, non-trivial molecule-cage correlations are generated. Vibrational coherences last for several vibrational periods of the embedded I₂, despite extensive dissipation to the Kr lattice. The computationally cheaper G-MCTDH approach is able to reproduce the detailed features of the absorption spectrum, autocorrelation function and subsystem density of the I₂Kr_n system, providing therefore a correct description of the dissipation mechanism.[8] The method is implemented in in-house codes, and is used to simulate and interpret nonlinear optical signals of high-dimensional dihalogen/host models from first principles. In the example of the figure, the I₂ chromophore is prepared in a 'Schrödinger's cat' superposition of two wave packets in the electronic B state; the time-resolved coherent resonance Raman signal is calculated and used to monitor vibrational decoherence.[4,5,8]



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This abstract was scaled because it exceeded the allowed page size.

Robust periodic Fock exchange with atom-centered Gaussian basis sets

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In this talk we present a robust implementation of the periodic Fock exchange for atom-centered Gaussian-type orbitals (GTOs). We discuss the divergence, appearing in the formulation of the periodic Fock exchange in case of a finite number of k-points, and compare two schemes that remove it. These are the minimum image convention (MIC) and the truncated Coulomb interaction (TCI) that we use here in combination with k-meshes. We show that four-center integrals of GTOs with nonvanishing angular momentum can exhibit a strong increase in absolute value at the cutoff radius R_c in the TCI scheme. Similar artifacts are seen in the exchange and density matrices of Hartree-Fock (HF) calculations for TCI, but not for MIC. At semiconducting and insulating systems we show that both MIC and TCI yield the same energies for a sufficiently large supercell or k-mesh, but the self-consistent field (SCF) algorithm is more stable for MIC. We therefore conclude that the MIC is superior to TCI and validate our implementation by comparing not only to other GTO-based calculations, but by demonstrating excellent agreement with results of plane-wave codes for sufficiently large Gaussian basis sets.

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The accurate computation of molecular properties using multiresolution analysis

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The formalism of Multiresolution Analysis (MRA) allows the computation of molecular properties at the limit of the complete basis. The real-space nature of MRA requires the reformulation of all working equations in first quantization. In this talk the general method of computing standard quantum chemical properties, e.g. energies, gradients, hessians, excitation energies, is presented and examples are given. Correlated methods, such as MP2 or CC2, require special care for the removal of the electronic singularities, whose presence would otherwise make computations on a 6-dimensional grid intractable. Diagrammatic techniques for deriving Coupled-Cluster equations may be used in MRA with only minor reinterpretations of the diagrams. The precision and the performance of MRA will be discussed, in particular with respect to CC2 ground and excited states[1, 2] and nuclear second derivatives for DFT.[3]



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Accurate core-level spectra from *GW*: An efficient approach within a localized basis

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We present a new, accurate method for computing X-ray photoelectron spectra (XPS) based on the GW approximation that overcomes the limitations of density functional theory (DFT) approaches. Inner-shell spectroscopy is an important tool to characterize molecules, liquids and adsorption processes at surfaces. Accurate computational methods to predict core excitations are therefore essential to support the interpretation of experimental spectra. Green's function theory in the GW approximation has become the method of choice for addition and removal energies of valence electrons in solids [1, 2] and is now increasingly being applied to molecules and clusters [3, 4]. However, GW core-level spectroscopy has thus far received almost no attention. In most GW implementations, the self-energy is typically computed in the imaginary frequency domain followed by an analytic continuation to the real frequency axis. However, the analytic continuation becomes highly inaccurate for frequencies far away from the Fermi level and is not suitable for the computation of core excitations. Thus, we evaluate the self-energy on the real-frequency axis using the contour deformation technique in combination with a local basis. We implemented this method in the all-electron code FHI-aims and optimized it for massively parallel execution. Our method reproduces the features of the self-energy perfectly compared to the fully analytic implementation in Turbomole. Our benchmark studies for small and mediumsized molecules show that the computed core-level binding energies deviate on average less than 0.5 eV from experiment outperforming the DFT-based Delta Self-Consistent Field (Δ SCF) approach.

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Inelastic X-ray scattering amplitudes in the ADC/ISR framework

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The development of 4th generation synchrotron radiation sources has led to rapid recent development in non-linear X-ray experiments like resonant inelastic X-ray scattering (RIXS) spectroscopy. State of the art RIXS experiments with ultra-high resolution create a high demand for theoretical support in the analysis of the complex spectra.

Here, we present an *ab initio* method to simulate RIXS cross-sections based on the Kramers-Heisenberg-Dirac (KHD) formula in the framework of the algebraic diagrammatic construction (ADC) scheme and the intermediate state representation (ISR) [1]. In contrast to commonly used approaches, restricted to selected channels, our *ansatz* allows for the evaluation of the <u>full</u> electronic part of the scattering amplitudes. Our results are in excellent agreement with experimental findings. The quantitative analysis via the full summation of the KHD formula in a closed matrix form reveals that while the resonant channels dominate, non-resonant scattering contributes significantly to the spectral features.



Figure 1: Inelastic X-ray scattering spectra of gas phase methanol. Simulated and recorded [2] at the resonance frequency ω of the second core-excited state. RIXS: peak dominated by resonant channel; NIXS: peak dominated by non-resonant channel

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8. Poster Abstracts

8.1. Poster Session A

Ρ1

Hydrotrope-Assisted Solubilization of Sparingly Soluble Drug Molecules in Water

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ABSTRACT: Hydrotropes are important class of molecules that enhance the solubility of an otherwise insoluble or sparingly soluble solute in water. Besides this, hydrotropes are also known to self-assemble in aqueous solution and form aggregates. It is the hydrotrope aggregate that helps in solubilizing a solute molecule in water. In view of this, we try to understand the underlying mechanism of self-aggregation of different types of hydrotropes in water by using classical molecular dynamics (MD) simulation. We further extend our study to explore the hydrotropic action of these hydrotrope molecules towards the solubility of different sparingly soluble orally administered drugs in water.

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Р3

Nonlinear-Response Properties in a Simplified Time-Dependent Density Functional Theory (sTD-DFT) Framework: Evaluation of the First Hyperpolarizability

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Recent developments in nonlinear imaging microscopy show the need to implement new theoretical tools able to characterize nonlinear optical properties in an efficient way. For secondharmonic imaging microscopy (SHIM)[1], quantum chemistry could play an important role to design new exogenous dyes with enhanced first hyperpolarizabilities or to characterize the response origin in large endogenous biological systems. Such methods should be able to screen a large number of compounds while reproducing their trends and to treat large systems in reasonable computational times. To fulfill these requirements, we present a new simplified timedependent density functional theory (sTD-DFT)[2] implementation to evaluate the first hyperpolarizability where the Coulomb and exchange integrals are approximated by short-range damped Coulomb interactions of transition density monopoles. For an ultra-fast computation of the first hyperpolarizability, a tight-binding version (sTD-DFT-xTB)[3] is also posed. We challenge our implementation on three test cases: typical push-pull π -conjugated compounds[4], fluorescent proteins[5], and a collagen model[6], which were selected to model requirements for SHIM applications. For push-pull systems, considering a frequency-dispersion below 1.0 eV, the sTD-DFT results are very similar to TD-DFT ones while the computational cost is drastically decreased. The sTD-DFT-xTB method shows its ability to screen a large set of compounds, qualitatively and inexpensively. Considering the fluorescent proteins, sTD-DFT-xTB method was able to reproduce the trends with respect to ONIOM MP2:HF calculations. For the collagen model, sTD-DFT-xTB method was able to provide a β frequency dispersion similar to the ONIOM LC-BLYP: HF one with a static β_{HRS} only 8% lower, showing the capability of sTD-DFT-xTB to treat ultra-fast complicated electronic properties in large biological systems.

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Ρ5

Biological applications from coupled cluster frozen density embedding

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For molecules in complex environments frozen-density embedding (FDE) can be used to avoid the scaling of conventional supermolecular *ab-initio* calculations, resulting in a linear scaling with respect to the number of molecules. One particularly efficient ansatz is RI-CC2–in–DFT, in which the second-order approximate coupled-cluster RI-CC2 method is employed for the molecule of interest while the environment is calculated using density-functional theory (DFT). For this ansatz and related methods such as RI-ADC(2)–in–DFT, analytical excited-state response properties are derived rigorously using a Lagrange-based formalism and have been implemented in the KOALA program. [1] The accuracy of excited-state geometries is assessed in selected case studies and it is shown that the new method can be used to investigate a retinal chromophore in a biological model environment comprising 32 molecules with 366 atoms in total on a standard compute node within a couple of days, enabling the study of biological model systems in ground and excited states using *ab-initio* methods as routine applications.



- Figure 1: Rhodopsin model consisting of 366 atoms with the effective solvent-accessible surface as computed using the RI-CC2–in–DFT method. [2, 3]
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Ρ7

A theoretically conceived photochemical pathway to solar water splitting using carbon nitride chromophores

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Recently, polymeric carbon nitride materials have attracted vast interest in the field of photocatalytic water splitting with visible light. They consist of earth abundant materials, are completely photostable and can split water into hydrogen and oxygen, albeit so far with low efficiency. The underlying mechanism is, however, not understood. Using excited-state wavefunction-based electronic-structure calculations and considering pyridine, triazine and heptazine (tri-*s*-triazine) as model chromophores, we propose a biphotonic photochemical cycle for water-splitting [1-3]: First, we show that H-atom transfer from water to a peripheral N-atom of the photoexcited chromophore is a low-barrier process, resulting in the hydrogenated chromophore and a hydroxyl radical in their electronic ground states. Analysis of orbital energies shows that the H-atom transfer reaction is driven by a hole transfer from the chromophore to the hydrogen-bonded water molecule. The predicted hydroxyl radicals have recently been detected by fluorescence spectroscopy with the help of hydroxyl radical scavengers [4]. In the second step, the excess H-atom is detached from the reduced chromophore by the absorption of a second photon, regenerating the catalyst. Thus, a water molecule is split into a hydroxyl radical and an H-atom in a bi-photonic process.



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Ring-Polymer Molecular Dynamics for Photochemistry

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During the last decade the Ring-Polymer Molecular Dynamics (RPMD) approach has proven to be an efficient method to approximately simulate quantum mechanical effects in chemical systems. Based on the path integral formulation, RPMD incorporates quantum effects using classical trajectories in an extended ring-polymer phase space. It exhibits appealing features including preservation of detailed balance, being exact in several limiting cases and it can be run efficiently exploiting techniques known from molecular dynamics. However, the initial formulation of RPMD is missing two important pieces to describe photochemical processes: it is limited to the calculation of correlation functions associated with the equilibrium Boltzmann distribution and it also does not allow for the treatment of non-Born-Oppenheimer effects. I will present the extension of the RPMD approach to simulate processes with non-equilibrium initial conditions. Furthermore, I will introduce ideas to treat non-Born-Oppenheimer effects within RPMD. The prospects of combining these developments to describe photoexcited processes is investigated.

What we can learn from comprehensive benchmark studies: insights for method developers and users

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After its publication in 2011, the GMTKN30 benchmark database for general main-group thermochemistry, kinetics and noncovalent interactions quickly became an invaluable tool for users and developers to assess the accuracy of electronic-structure methods [1]. In this presentation, I will summarise our latest collaborative efforts in this area, which culminated in the new GMTKN55 database [2]. Compared to its predecessor, GMTKN55 allows assessment across a larger variety of chemical problems and offers reference values of significantly higher quality, with 1505 relative energies based on 2462 single-point calculations. I will demonstrate the importance of better reference values in benchmark studies and re-emphasise the need for London-dispersion corrections in density functional theory (DFT) treatments of thermochemical problems — including for Minnesota methods, which do not describe London dispersion despite common belief [2, 3]. Up to date, we have established a comprehensive overview of more than 325 variations of dispersion-corrected and uncorrected density functional approximations, which collectively constitutes one of the most comprehensive DFT benchmark studies carried out [2, 4, 5]. The obvious benefit of our GMTKN55 studies is that we can give clear recommendations to DFT users, hopefully changing their future computational strategies. However, our data also provide valuable insights for method developers, and I will highlight this additional benefit of GMTKN55 with the help of two examples that represent some developers' current interests:

- (a) Making van-der-Waals DFT computationally more efficient without compromising its potential to describe noncovalent interactions [4].
- (b) Providing the first fair comparison between semi-empirical and non-empirical double-hybrid density functionals with the latter being a highly active research area to once and for all answer the question which of the two approaches is more robust and reliable [5].
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What can we learn about the solvation of ions in bulk water by studying ion-water clusters as a function of cluster size?

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Small ion-water clusters are excellent model systems to study microsolvation and its impact on spectroscopic properties. It is, however, unclear to what extent such small clusters are meaningful minimal models to understand bulk ion solvation, keeping in mind that it is well established from experiments that the effect of ions on the water structure is largely limited to their first solvation shells. In this study we have undertaken an extensive density functional-based ab initio molecular dynamics study of various equilibrium structures and the corresponding THz spectra of small water clusters of Na⁺, namely Na⁺-(H₂O)_n, n = 4-8,10,12,14,17 and 20. In this context, the issue of omitting empirical dispersion interaction corrections between Na⁺ and H₂O, turns out to be intricate with reference to wavefunction-based benchmarks on structure and relative energetics. Ab initio molecular dynamics simulations are performed at 300 K temperature in order to probe the structural dynamics of microsolvated clusters in direct comparison to the same ions at bulk solvation conditions. Additionally, their THz spectra are computed and also decomposed in terms of well-defined intra- and inter-molecular contributions including solute-solvent couplings in order to compare those to what has been found in the bulk solvation limit. Finally, based on the THz vibrational response due to H-bonded water molecules around Na⁺ in small clusters, it is established that even such medium-sized gas-phase clusters are not representative models to understand bulk solvation of Na⁺.

Neural Network Potentials for Solvation: Protonated Water Clusters in Superfluid Helium

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Superfluid helium is a highly fascinating liquid where quantum effects are pervasive. Its many interesting properties such as zero viscosity and vanishing friction can all be explained by the Bose-Einstein-like condensation of ⁴He particles below 2.17 K in the bulk phase. Helium also forms nanodroplets that feature superfluid behavior and can be used to solvate guest molecules. This allows one to examine for example hydrogen bonded clusters in a gentle, ultracold environment by infrared spectroscopy as performed in HENDI experiments [1].

However, at temperatures on the order of one Kelvin, nuclear quantum effects govern the properties and can not be neglected. Here quantum simulation techniques employing path integrals can be used to include the quantum nature of the nuclei exactly [2]. Only recently these techniques were extended to treat reactive solute species by coupling bosonic PIMC simulations of helium to PIMD simulations of the solute [3, 4]. This allows one to study systems such as protonated water clusters including their full reactivity solvated by superfluid helium. These simulations, however, require very accurate potentials for the description of the solute as well as to link the two regimes [5, 6].

Here we show how artificial neural networks [7, 8] can be applied to develop potential energy surfaces of protonated water clusters and interaction potentials [9] for the solvation of these clusters by superfluid helium. The intrinsic nature of neural networks does not only allow to represent the reference coupled cluster energies with very high accuracy, but also provides the opportunity to easily identify missing points in configuration space and hence to keep the number of reference calculations to a minimum. It thus provides a quasi-automated way to quickly generate on demand specific molecule-helium interactions at the coupled cluster level. This offers the opportunity for an unbiased and elegant access to potential energy surfaces and solute-He interaction energies and thus to push forward our fundamental knowledge about non-covalent interactions.

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Bonding and stability analysis of tetravalent f-element complexes with mixed N-, O-donor ligands

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The contribution of the f-orbitals leads to a very rich chemistry of the f-elements[1] where it is known that this contribution is less important for lanthanides. Of special interest is the influence of these orbitals on the bonding character of actinides and lanthanides with organic ligands reflecting natural bonding motifs.

This study shows the different bonding behaviour of tetravalent f-elements with Schiff bases, like salen (see Fig. 1) and derivatives, by means of real-space bonding analysis. This includes the popular quantum theory of atoms in molecules (QTAIM), plots of the non-covalent interactions (NCI)[2] and density differences complemented by natural population analysis (NPA). Thermodynamic calculations on the stability of these complexes are presented. The obtained results are a direct consequence of the different interaction strengths of the f-elements.

First studies reveal a strong interaction of the actinides, i.e. Th to Pu, with the oxygen of salen characterized by a high electron density concentration between the atoms. In contrast, the interaction between the actinides and the nitrogen of salen is much weaker.

By acquiring knowledge about the different behaviours of bonding and complexation it is possible to understand the chemical properties of the f-elements and predict yet unknown complexes.



Figure 1: Molecular structure of $[MCl_2(salen)(thf)_2]$, with M = Ce, Th, Pa, U, Np, Pu.

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Why does my back hurt: A systematic study of OCS complexes.

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Despite being a known nerve agent, carbonyl sulphide (OCS) is a gas that is perhaps overstudied in rotational spectroscopy. However, some of its complexes, such as the Xe–OCS complex, have not been previously investigated, while large uncertainties remain in the experimental structure of the He–OCS complex. Therefore, we present a systematic computational study of the rare gas (Rg) – OCS complexes, including the He, Ne, Ar, Kr, Xe, and Hg dimers, supported by an experimental investigation of the Xe–OCS dimer.

An accurate experimental ground state averaged structure (r_0) and a near-equilibrium structure (r_m) was obtained for the Xe–OCS complex using Fourier-transform microwave spectroscopy. These structures are compared to the semi-experimental equilibrium structure (r_e^{SE}) obtained for Xe–OCS analogously to other Rg–OCS complexes [1], including the Ne, Ar, Kr, and Hg complexes.

The treatment of the anharmonic vibrational contributions to the ground state-averaged structures is discussed by comparing our previous results [1] from dispersion-corrected doublehybrid density functional theory [2, 3] with correlated wavefunction methods extrapolated to the complete basis set limit.

Finally, a detailed analysis of the potential energy surface of the OCS complexes with He, Ne and Ar has been performed using symmetry-adapted perturbation theory [4], allowing us to investigate the contributions that lead to an increase in the binding energy in the complexes down the group. The accurate potential energy surface of the He–OCS dimer, supported by the equilibrium and ground-state average geometry obtained from correlated wavefunction theory, allows us to discriminate between the two proposed experimental structures [5, 6].

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Modelling the structural and optical properties of supramolecular arrays adsorbed on hexagonal boron nitride: the effect of non-covalent interactions

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Two-dimensional supramolecular assembly of organic molecules, which can be achieved on a wide range of different substrates, provides a highly flexible route to control the spatial organization of adsorbates and the chemical functionality of a surface.

We present results of our recent computational studies based on the density functional theory, which were focused on modelling the structural and optical properties of different molecular arrays adsorbed on hexagonal boron nitride. [1,2]

We discuss how non-covalent interactions influence the structure of adsorbed perylene and porphyrin derivatives in their ground and excited states and the corresponding absorption and fluorescence energies.

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Vibrational Spectroscopy and Dynamics of the Hydroxylated α -Al₂O₃(0001) Surface with (and without) Water: Insights from Ab Initio Molecular Dynamics

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Understanding water interactions with metal oxide surfaces [1] (such as aluminum oxide, Al_2O_3) is of importance both for fundamental reasons and for technological applications. To unravel the details of such interactions, spectroscopic methods in the form of vibrational (IR) spectroscopy or, as surface-sensitive tool, Vibrational Sum Frequency (VSF) generation spectroscopy [2,3] are powerful experimental techniques which have been applied with great success.

However, the interpretation of vibrational spectra is typically hard and requires theoretical support. On the simplest level of theory, simple Normal Mode Analysis (NMA) is performed in order to do so. This approach lacks inclusion of anharmonicities, thermal motion, and spectroscopic selection rules, however, which can be decisive. These features are accessible, in principle, by (classical) correlation function approaches [4] which can be evaluated by Ab Initio Molecular Dynamics (AIMD).

Here we apply recently proposed, efficient methods based on velocity-velocity autocorrelation functions (VVACFs) [5] to compute vibrational spectra (IR and VSF) of hydroxylated α -Al₂O₃(0001) surfaces with and without additional water [6]. We compare the validity of NMA and of Vibrational Density of States (VDOS) curves to predict / interprete IR and VSF spectra at finite temperature which we determine by VVACF-based AIMD. Further, a detailed assignment of vibrational signals is given, with special emphasis on the key role played by surface OH bonds, their dynamical behaviour and the effects brought in by H₂O adsorption. When possible, a connection to recent experiments [7,8] is made.

Further theoretical efforts are spent to address the vibrational relaxation and lifetimes of surface OH-species, whose dynamics is followed by pump-probe VSF-measurements. We again employ AIMD simulations to investigate the structural properties of hydroxylated α -alumina surface which can influence the energy pathways of excited OH bonds. We then propose lifetimes in qualitative agreement with time-resolved experiments [9].

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Linear and Quadratic icMRCC approximations

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Internally contracted multireference coupled-cluster (icMRCC) allows for the description of both dynamic and non-dynamic correlation within the molecular wavefunction. Capturing both correlation effects is essential in accurately describing chemical phenomena such as bond breaking and formation, excited states, radical species and molecular complexes. With size extensivity and orbital invariance, icMRCC provides a rigorous way of combining the properties of single-reference coupled-cluster into a multireference context.

However, due to the addition of the active orbital subspace, the number of unique terms that are required to be evaluated in the energy and amplitude equations grows rapidly, even after truncation of terms quadratic in the amplitudes. This can be up to 10^5 times more terms than the corresponding single-reference coupled-cluster methods.

As a result, linear and quadratic approximations have been developed which aim to decrease the computational expense and increase the scope and usage of icMRCC to larger molecular systems. These have been inspired by older methods, like the well known CEPA(0) approximation, and justified using many-body perturbation theory.

These new approximations are benchmarked against FCI, for a series of diatomic systems, to investigate accuracy and the contribution individual terms have in the amplitude and energy equations. The chemistry of larger molecular structures are also investigated, which suggests the future use of these approximations.

The Master Factors Influencing the Potency of BACE-1 Alzheimer Inhibitors: Computational & Molecular Docking Studies

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Density functional theory (B3LYP/6-31G (d)) is performed to study the effect of molecular and electronic structures of the investigated BACE-1 Alzheimer inhibitors on their biological activities and discuss the correlation between their inhibition efficiencies and quantum chemical descriptors. IC₅₀ values of the investigated compounds are mostly affected by the substituted R₂ Phenyl (S₂) moiety. The calculations show that the presence of electron withdrawing group increases the biological activity. SAR studies show that the electronic descriptors, E_{HOMO}, Δ E, lipophilicity, hardness and ionization potential index, are the most significant descriptors for the correlation with the biological activity. Molecular docking simulation is performed to explain the mode of interaction between the most potent drug and the binding sites of BACE-1 target. A good correlation between the experimental and theoretical data confirms that the quantum chemical methods are successful tools for the discovery of novel BACE-1drugs.



Low-lying Electronic States of the Molecules AB_n (A = Sc - Ni, B = Cu/Ag/Au, n = 1, 2)

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Small molecules formed by the atoms of the d-block elements are building blocks for catalytically and photochemically active systems, for nanostructured materials, and for electronic and magnetic devices that receive considerable attention in both fundamental and applied research.[1] **Diatomic Molecules** *AB*: Full potential energy curves, in both Λ -S and Ω representations, of the low-lying electronic terms of the diatomic molecules *AB* (*A* = Sc – Ni, *B* = Cu/Ag/Au) have been constructed using the multi-reference configuration interaction (MRCI) techniques. Scalar relativistic effects were included by use of the spin-free Douglas-Kroll-Hess (DKH) Hamiltonian, and spin-orbit coupling was subsequently incorporated perturbatively *via* the spin-orbit terms of the Breit-Pauli Hamiltonian based on the CASSCF wavefunctions.

Triatomic Molecules AB_2 : Λ -S potential energy surfaces, $E(\theta, r; {}^{2S+1}\Gamma)$ and $E(r_1, r_2; {}^{2S+1}\Gamma)$, for the ground and low-lying electronic states of the triatomic molecules AB_2 have been determined at the MRCI/DKH level of theory and using 3D spline interpolation over ≈ 230 symmetryunique *ab initio* points. $E(\theta, r; {}^{2S+1}\Gamma)$, where θ is the $\angle BAB$ angle ($40^{\circ} \le \theta \le 180^{\circ}$), r is the *B*-*A* (or *A*-*B*) distance $(2 \le r \le 3 \text{ Å})$, and ${}^{2S+1}\Gamma$ is the given A-S electronic state, provides an unbiased representation covering the C_{2v} and $D_{\infty h}$ symmetries corresponding to the bent and linear B–A–B structures, respectively. $E(r_1, r_2; {}^{2S+1}\Gamma)$, where r_1 is the A–B distance and r_2 is the *B*-*B* distance ($\approx 2.2 \leq r_1, r_2 \leq \approx 3.3$ Å), represents the $C_{\infty y}$ symmetry corresponding to A-B-B. These potentials were assumed to possess the global minimum and allowed us to determine (predict) the potential minimum (ground state) as well as several low-lying stationary points (isomers). Although, regardless of the electronic states, the energy differences between the low-lying isomers are miserably small for some cases, our accurate description of the electronic wavefunctions via correlating all valence electrons at the MRCI level of theory provides a unique broad representation. This, at the same level of theory, enables us to compare energies of different symmetries $(D_{\infty h}, C_{\infty \nu}, C_{2\nu})$, to estimate the transition barriers for a few symmetry-restricted reaction channels, and to relate the energy of the ground state to that of various supreme asymptotes: $AB(X^{2S+1}\Lambda) + B(^2S)$, $A(^{2S+1}L) + B_2(X^1\Sigma_g^+)$, and $A(^{2S+1}L) + B_2(X^1\Sigma_g^+)$ $B({}^{2}S) \times 2$. Similar to diatomic molecules AB, results of which are the cornerstones for those of AB_2 , strong similarities exist between the electronic structure of ACu_2 , AAg_2 , and AAu_2 .

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On the automatic computation of global intermolecular potential energy surfaces for non-covalently bound systems

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A detailed knowledge of the topography of a Potential Energy Surface (PES) is a highly desirable prerequisite for the simulation of any dynamical process. Topography on its own, however, does not fully determine the (quantum) behaviour of a system and dynamical calculations become mandatory [1, 2]. Characterisation of the topography of a PES is a tedious task and, for large dimensional systems, not an evident one. In recent years, a series of methodologies for the automatic determination of stationary points for *covalently* bound systems have been proposed. Among them, the so-called Transition State Search using Chemical Dynamics Simulations (TSSCDS) [3] relies on the efficient sampling of configuration space using a semiempirical level of theory combined with a graph-theory (adjacency matrix) based identification of guess structures to transition states (TS). The latter are subsequently optimized at an appropriate level of theory and Minimum Energy Paths are computed, thus generating the so-called reaction network (RXN). We have recently developed the vdW-TSSCDS method, a variant of TSSCDS, specifically designed for the automatic characterization of PESs of non-covalently bound systems [4]. The key idea has been the redefinition of the adjacency matrix in block-diagonal structure where diagonal blocks correspond to isolated fragments and off-diagonal blocks to intermolecular interactions. We have successfully applied this approach to semirigid-monomer complexes (e.g. benzene-water) as well as to reactive systems (e.g. naphthalene cation plus hydrogen). We present the vdW-TSSCDS method and its application to the construction of global PESs. More specifically, PESs in the form necessary for high-dimensional quantum dynamical calculations in the context of the Multiconfiguration Time-Dependent Hartree (MCTDH) method [5]. To this end, the information of the RXN is used to reparametrize a semiempirical Hamiltonian which is interfaced to the tensor decomposition algorithm Multigrid POTFIT [6]. This provides the PES in the correct mathematical form for MCTDH.

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Dispersion-Corrected Noncovalent Interaction Energies from a Hybrid First-Principles–Gaussian Process Model

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We apply Gaussian process (GP) regression to correct for systematic errors in noncovalent interaction energies derived from first-principles models [1]. Unlike other established machine learning methods, GP regression does not only provide predictions/corrections but also estimates the associated uncertainty, which can be used to decide whether a correction for a new (supra)molecular structure is reliable or not. Analogously to the popular class of semiclassical London dispersion correction models, our GP model is trained on differences between approximate and reference interaction energies, here, obtained from PBE-D3(BJ)/ma-def2-QZVPP and DLPNO-CCSD(T)/CBS calculations, respectively. We introduce a data set containing noncovalent interaction energies for 1250 molecular dimers, which resemble those systems contained in the S66 database. Our systems do not only represent equilibrium structures, but also dimers at shorter and longer distances as well as different orientations and conformations. As with many physics-based machine learning models of chemical phenomena, the independent variables (features) of our GP model represent atomic interactions. We additionally require that the features are exclusively derived from the approximate model to be corrected. Accordingly, we only add information to our features that is contained in the D3(BJ) model, rendering our GP predictions essentially "self-corrected" DFT-D3(BJ) energies. Training our GP model on feature-energy pairs of about 100 dimers, we find an up-to-10-fold improvement over PBE-D3(BJ) interaction energies for the remaining dimers. We also find that — for a given application domain — our GP-corrected energies are insensitive toward the actual parametrization of the D3(BJ) model, which is in clear contrast to DFT-D3(BJ)-corrected energies [2]. Given that the GP-estimated uncertainty for a correction is above a user-defined threshold, one can simply update the GP model by adding the corresponding feature-energy pair to the training set, which will improve corrections for similar systems. This important quality assessment, which established London dispersion correction models lack, renders our GP approach suitable for an on-the-fly improvement of noncovalent interaction energies.

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Photochemistry of Organic Molecules in Ionic Environment: Experimental-Theoretical Investigation of Aerosol Models

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Aerosols are small particles composed mainly of organic molecules, inorganic ions, and water. They play an important role in the atmosphere, form haze, fog or smog, and affect human health. They also represent a tangible example of the influence of the environment on adsorbed organic molecules. It is well known that aerosol chemistry is governed by the particle composition [1]. However, aerosol photochemistry on the molecular level is largely unexplored.

In this contribution, we present mass spectrometric investigations performed on an FT-ICR spectrometer, coupled to a tunable UV/VIS Optical Parametric Oscillator. Ab initio calculations (TDDFT, EOM-CCSD, CASSCF, MRCI along with reflection principle for spectra modelling) are performed to explain the experimental findings and to develop a molecular level understanding of photochemical processes in aerosols. We discuss the photochemistry of the glyoxylate anion and its change after complexing with NaCl (Figure 1) [2], showing that the ionic environment supports the CO_2^{-*} dissociation channel and stabilizes this radical ion in the cluster. We also investigate IR and UV spectra of camphor, formate, and pyruvate adsorbed on NaI clusters that enable us to analyze the interaction between the organic molecule and the salt cluster [3].



Figure 1 – Photochemistry of glyoxylate anion, Na.glyoxylate cluster and $[Na_6Cl_4.glyoxylate]^+$. Calculated at the CASSCF(6,6)/def2-TZVP,ECP(Na,Cl) level of theory (lines) and recalculated at the respective MRCI level (crosses).

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Proton-irradiated ice: electronic excitations via Real-Time TDDFT

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Ion irradiation of water systems is receiving an increasing attention due to many important applications, such as radiation damage of biological tissues or radiation treatment of tumors, both cases involving systems with a high content of liquid water.

For the case of ice, describing its interaction with highly energetic particles at the atomistic and electronic scale is of paramount importance to understand many astrophysical/chemical processes taking place in interstellar dust, comets, asteroids and satellites which are exposed to such particles due to the action of solar wind, cosmic rays or strong magnetospheres.

Here I will show the results of Real-Time Time-Dependent-DFT calculations [1] where the irradiation of ice with highly energetic protons is simulated in real time via Ehrenfest MD, following the excitations of the electronic subsystem in the ice sample promoted by the passing of the proton projectile. This allows a deep understanding of the process, allowing us not only to precisely compute the energy absorbed by the target, but also to obtain a chemically intuitive picture of which kind of electrons in the system (either 'lone pairs' or 'bonding pairs' electrons) are more likely to get excited, ultimately leading to ionization of the ice target. The influence of factors such as the trajectory and energy of the incoming proton will be also disclosed, helping to fill a gap in the current experimental and theoretical knowledge of this process.



Figure 1: a) Excitation distribution at different instants $P(E)_t$ in comparison to the total DOS of the unperturbed ice sample. b) Electronic density difference (yellow/blue: charge accumulation/depletion) of the excited ice system upon irradiation with a 50 keV proton (green) with respect to the ground state.

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Deep Eutectic Solvents: Similia Similibus Solvuntur?

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Deep eutectic solvents, mixtures of an organic compound and a salt with a deep eutectic melting point, are promising cheap and eco-friendly alternatives to ionic liquids. Most popular are mixtures of choline chloride, which is a provitamin produced on the megaton scale and forms a deep eutectic solvent with diverse cheap organic compounds. Within our contribution, we will present the results of the first ab initio molecular dynamics simulation studies of deep eutectic solvents focussing on the origin of the low melting point of reline, a mixture consisting of choline chloride and urea in a 1:2 ratio.

The negative charge transferred from the anion to the organic compound is overall negligible and, thus, cannot contribute to the low melting point.[1] However, not solely hydrogen bonds allow similar interactions between both constituents. The chloride anion and the oxygen atom of urea also show a similar spatial distribution close to the cationic core of choline due to a similar charge located on both atoms. As a result of multiple similar interactions, clusters migrating together cannot be observed in reline which supports the hypothesis similia similibus solvuntur. In contrast to previous suggestions, the interaction of the hydroxyl group of choline with a hydrogen bond acceptor is overall rigid. Fast hydrogen bond acceptor dynamics is facilitated by the hydrogen atoms in the trans position to the carbonyl group of urea which contributes to the low melting point of reline.[2]

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Taking Advantage of Host-Guest Interactions to Make the Undetectable Detectable in ¹⁹F NMR

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Host-guest interactions often are dominated by noncovalent interactions between the constituent components. Recently, we used the dynamic nature of the host-guest interactions between cucurbit[n]uril (CB[n]) hosts – which form a cylindrical cavity – and fluorinated small molecules (in particular, halothane – 2-bromo-2-chloro-1,1,1-trifluoroethane) to demonstrate how one can use magnetization transfer in a ¹⁹F NMR study to detect otherwise undetectable species.[1] The transient nature of the guest molecule in the CB[n] channel allows for transfer of magnetization to the free guest population to allow detection of the hosted guest. In such a manner, a signal amplification of 100-fold was achieved.[1] This was followed up by demonstrating how exchange rates can be measured using this technique.[2]

Here we present our results into the study of the host-guest nature of these and related complexes and the exchange of the guest molecules. Various methods were used, including density functional theory, Grimme's extended tight-binding method for noncovalent interactions (GFN-xTB)[3] and Grimme's quantum mechanically derived force field (QMDFF).[4]



Figure 1. Using magnetization transfer to detect the signal of halothane@CB[8] in ¹⁹F NMR (source: reference [1]).

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QM/MM Photodynamics of Retinal Proteins with the OMx-MRCI Method

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The conjugated retinal chromophore is the photoactive component in various receptor proteins found in Nature. Its all-trans form e.g. steers proton pumping in bacteriorhodopsin (bR) or cation-channel opening in channelrhodopsins (ChRs). 11-cis retinal triggers vision in mammalian and invertebrate rhodopsins (Rh). Absorption properties and reactivity of retinal are tuned through electrostatic and steric interactions with its protein binding pocket. After photoexcitation, the chromophore undergoes ultrafast and efficient all-trans to 13-cis (bR, ChR) or 11-cis to all-trans (Rh) photoisomerization. This structural change induces rearrangements in the protein that activate it for the corresponding function. A thorough understanding of the chromophore-protein interactions is necessary to suggest sensible modifications for optimized biotechnical or biomedical applications. The investigation of retinal photodynamics so far has been pursued with CASSCF or CASPT2 ab initio strategies. These methods can provide accurate results [1,2] but are computationally highly demanding. We have tested the suitability of the semiempirical OMx-MRCI method developed by Thiel et al. [3] for simulating retinal photodynamics within a QM/MM environment. A newly developed interface to the COBRAMM QM/MM suite [4] allows us to perform surface hopping simulations using the semiempirical MNDO package and the molecular mechanics program Amber. [5] With this methodology we have investigated the photodynamics of retinal in bovine rhodopsin, the ChR chimera C1C2, bR and anabaena sensory rhodopsin.

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Proton Mobility in Aqueous Systems: Combining ab-initio Accuracy with Millisecond Timescales

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We present a multiscale simulation of proton transport in liquid water, combining ab-initio molecular dynamics simulations with force-field ensemble averaging and kinetic Monte-Carlo simulations. This unique Ansatz allows for ab-initio accuracy incorporating the femtosecond dielectric relaxation dynamics of the aqueous hydrogen bonding network, and bridges the time-scale gap towards the explicit simulation of millisecond diffusion dynamics.

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Local XA Spectroscopy: A Database Approach to Carbogenic Materials

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Carbogenic materials like Graphene Oxide (GO) quantum dots have proven to be a versatile material for interesting applications such as photocatalytic water splitting[1]. Due to the defectuous nature of GO derived materials[2], it has however not been possible yet to fully understand what structural features are causing their unique chemical and physical properties.

Bearing to the surrounding sensitivity of X-ray absorption (XA) spectroscopy, we establish a time-dependent density functional theory (TDDFT) approach to probe the constitution of specific atoms in model systems in a meaningful way. Here, we compute localized coreexcitation absorption spectra of carbon 1s orbitals at single atoms and correlate several hundreds of individual-atom spectra to their respective local chemical environments.

Since localized carbon K-edge XAS-spectra have shown to be surrounding sensitive to up to approximately three chemical bonds[3], we may use a multitude of model systems of relatively small size to produce a database of locally distinguishable spectra that each then represent a specific functionalization pattern. From this database we may then compose both experimental as well as theoretical spectra and thus identify prominent functional groups in even defectuous materials.

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Non-covalent interactions in switchable supramolecular systems

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In the realms of supramolecular chemistry we strive to mimic macroscopic devices on a microscopic level. Here we report a supramolecular system, a [3]rotaxane, capable of performing a mechanical motion at the nano-scale level similar to that of a friction clutch encountered in modern vehicles. This "molecular friction clutch" can switch between two locally stable geometries (clutched and declutched) via electrochemical oxidation and reduction. The key to understanding this property lies within the non-covalent interactions present in the molecule, depending on its overall charge state. Quantum chemical calculations were performed to support experimental findings and gather information not accessible by experiment. Particular attention was paid to the non-covalent interactions between the two TTF (Tetrathiafulvalene: marked in yellow in figure below) moieties attached to the structure as those were the key components for the switchability of the supramolecule.



Figure 1: Switching a redox-active [3]rotaxane between two locally stable geometries

A study of interaction between Au nano particles and some nanoscale surfaces

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Nano particles have been used as catalysts for a long time[1]. The decreaseing of size, besides increasing the surface area, is expected to make the catalytic active sites on the metal surface readily available to ariving reagents. Even noble metals such as gold in their decreased size to nanometer are used as catalysts[2]. In addition to, cobalt, and iron have also been utilized as catalyst in for preparing carbon and silicon nanotubes[3].In industrially catalytic application heat-stable Au-based catalysts is crucial role. So, in our work, we investigate stability of Au nanoparticles on the different nanoscale surfase (graphene, Si3N4, SiO2) using molecuoar dynamic simulation . Also thermodynamic properties e.g melting point, heat capasity and thermal conductivity are measured for alone Au nanoparticles and with surfaces. Results show melting point for Au nanoparticles with surface decrease compare to alone nanoparticles (figure1). Changes of heat capacity with increasing temprature show transition phase is first order (figure 2).Thermal conductivity decrease with increasing temprature for all Au based surfaces(figure3).



Figure1. Dependence potential energy on temperature in Au and Au-based

Figure2. Dependence Cv on temperature in Au and Au-based



Figure3. Dependence KAPPA_(Phononic) on temperature in Au and Au-based

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Revisiting the Canonical Product Format for Full Configuration Interaction

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Currently, there is strong interest in low-scaling electronic structure methods that allow the accurate treatment of extended systems. This can be achieved by local correlation methods, which have matured to a point where they can routinely be applied in standard applications of single reference methods, e.g. DLPNO-CC or PNO-LCC[1]. The treatment of strongly correlated systems, however, that typically require methods like CASSCF, are still limited by the number of electrons that can be included in the computation. One possibility to compute larger systems is a stochastic solution as formulated within the framework of FCIQMC[2]. Another approach is to use tensor decompositions for the representation of the wave function. The matrix product state is a possible choice[3], which is commonly used in DMRG[4].

In this work we want to explore the potential of the canonical product (CP) tensor format for full configuration interaction (FCI) computations, an alternative having a low scaling with the number of electrons. In a recent proof-of-principle publication this combination was successfully applied to small systems[5]. The computation times are currently larger than standard implementations of FCI in quantum chemistry packages and it is an open question if system sizes can be reached, where the advantageous scaling of this method becomes decisive. We will address the advantages and disadvantages of various algorithms. Special attention will be given to avoiding rank reduction procedures, which have been the bottleneck of the first implementation[5]. An attempt will be presented to reduce the computing time by using configuration interaction singles and doubles to precondition the equations in the CP tensor format.

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Si(001) defects and their impact on surface reactivity

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The Si(001) surface is well known for its high reactivity towards nucleophiles as well as electrophiles [?]. This characteristic is a result of surface atoms recombining to tilted dimers with alternating lonepair- and unoccupied p-orbitals. Unfortunately, the resulting low chemical selectivity makes controlled patterning of the surface - as is desired for example in area-selective atomic layer deposition - rather challenging.

While the presence of defects is generally considered undesirable, purposely introduced defects may offer a remedy by locally altering reactivity. One such defect species is the missing dimer vacancy (DV), also known as 'A-defect' [?]. As a result of surface preparation techniques having matured to the point where a given sample is practically DV free [?], its electronic structure is not well studied.

We use density functional theory based bonding analysis [?] to gain mechanistic insights into the adsorption of small organic molecules at a DV site. In a preliminary study ethylene, acetylene and cyclooctyne are employed as model systems for unsaturated hydrocarbons and compared to our previous results for the ideal surface [?][?][?].

Furthermore, *ab initio* calculations show that the surface may be passivated with H_2 in such a way that the defect remains as the only reactive site.



Figure 1: Selective adsorption on a passivated surface with DV.

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Accurate Calculation of NMR Properties with Wave Function Based Methods

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Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most widely used analytical tools in organic and inorganic chemistry. The chemical shielding constants and nuclear spin-spin coupling constants obtained in NMR experiments yield valuable information on the chemical environment of the nuclei under consideration. However, NMR spectra become more and more complex with increasing system size, which necessitates the accurate quantum chemical calculation of NMR observables to unambiguously assign experimental peaks to structural motifs. Unfortunately, no quantum chemical method exists to calculate both observables accurately within acceptable computation time.

We have developed a general framework for the calculation of second derivatives of the energy with respect to the magnetic field and the nuclear magnetic moments, which yields the chemical shielding and nuclear spin-spin coupling tensors. This framework uses the pleasingly parallel approach of finite differences, thus allowing us to rapidly screen a plethora of wave function based methods for the calculation of NMR properties without the necessity to implement the analytical derivative expressions.

Our focus lies on Orbital-Optimized Møller-Plesset Second-Order Perturbation Theory (OO-MP2),[1, 2] since this method has been shown to be resistant to triplet instabilities, which constitute a severe problem for many wave function based methods when calculating nuclear spin-spin coupling constants. Hence, OO-MP2 holds great promise as a moderately expensive wave function based method to accurately calculate chemical shielding constants and nuclear spin-spin coupling constants. Our goal is to use new wave function based methods to generate high quality *ab initio* data to train a neural network that is able to predict NMR spectra of intrinsically disordered proteins.

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Time-dependent electron momenta from Born-Oppenheimer calculations

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The time-dependent expectation value of the electron momentum is zero if determined within the Born-Oppenheimer (BO) approximation. We show that one arrives at non-zero values, if the mean momentum is calculated from the time-derivative of the electronic coordinate. This is illustrated for the case of a coupled electron-nuclear motion in a one- and two-dimensional model system and also for an extended one-dimensional model with two electrons. Regarding a situation where the BO approximation is valid, we find that the BO results are in perfect agreement with those derived from the numerically exact calculations. This holds for cases where the involved wave packets are well localized and also if a large spreading of the probability density occurs.

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Ester-assisted folding of linear alkyl chains – a combined Raman and quantum chemistry approach

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When suspended in vacuum, linear alkanes assume a folded global minimum structure beyond a chain length $n = 17 \pm 1[1]$, largely driven by London dispersion forces. Raman spectroscopy in adiabatic gas expansions is highly suitable to study this conformational switch, which allows for benchmarking theoretical methods for chain polymers in terms of segment interaction and distortion[2–4]. Due to rather high barriers for conformational interconversion and the resulting kinetic hindrance in supersonic jet experiments, it is not easy to experimentally narrow down this critical chain length. By introducing a mid chain ester group, we expect to achieve a sharper transition between stretched and folded conformations, because some of the torsional barriers drop significantly. Exploratory investigations for methyl butanoate[5] and longer chain homologs are presented and analyzed in terms of folding motifs and conformational preference. Adequate computational levels for the description of the conformational landscape of long-chain aliphatic esters are discussed.

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REMP: A New Hybrid Perturbation Theory with Improved Prediction Capabilities

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We present a new hybrid perturbation theory that emerges from mixing the unperturbed Hamiltonians $\widehat{H}^{(0)}$ of the famous Møller-Plesset perturbation theory and the "Retaining the Excitation Degree Perturbation Theory". The latter one has been developed in our laboratory some years ago.^[1,2] Perturbation theory is a well-established tool for incorporating electron correlation into wavefunction methods at moderate cost. We carefully analysed the errors in the PT wave functions of several perturbation theories with respect to near Full-CI wave functions in terms of configuration state functions.^[3] Based on these findings we propose a new partitioning scheme which gives rise to results that are superior both to the parent methods as well as other well-established PT methods like SCS-MP2. The REMP model results from adding the unperturbed Hamiltonians of MP and RE in such a way that the one-electron part of the Hamiltonian is conserved:

$$\widehat{H}_{\text{REMP}}^{(0)} = (1 - A)\widehat{H}_{\text{RE}}^{(0)} + A\widehat{H}_{\text{MP}}^{(0)}$$

In contrast to SCS-MP2, REMP defines a class of proper perturbation series. It gives rise to wavefunctions which obey the electron-electron Kato cusp condition and have well-behaved spin properties. REMP contains only one empirical mixing parameter and no further scaling. Like the parent method, it is size consistent, size extensive and unitary invariant.

The main goal of the parameter optimization was to reproduce the Full CI wave function as close as possible at 2^{nd} order PT level. For practical applications, we also have been searching for Pauling points in the parameter space by means of comparing predicted geometrical parameters to experimental values. For $A \approx 0.1$ REMP outperforms current PT methods and many alternative singles-doubles wave function models regarding equilibrium bond lenghts and equilibrium harmonic frequencies.

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Application and Benchmarking of The New DFT-D4 Method

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Recently, we proposed an extension of the well-established DFT-D3 dispersion corrected density functional theory[1]. The new method, dubbed DFT-D4[2], has been developed in the frame-work of density functional tight binding (DFTB) together with the second parameterization for geometries, frequencies and non-covalent interactions (GFN) of the extend tight binding (xTB) Hamiltonian[3]. As the main new feature it takes electronic structure information into account which is absent in DFT-D3, while keeping most parts of the theory developed within the predecessor model. Notable features of the DFT-D4 are the explicit dependency of the dispersion energy on atomic partial charges from GFN2-xTB and the improved many-body dispersion treatment by an RPA-like energy expression to include dipole–dipole dispersion terms up to infinite order. The damping parameters of the model were determined for 67 standard density functionals enabling routine energy evaluations and geometry optimization with the available analytical gradient. DFT-D4 can keep up with the good performance of DFT-D3 for main group chemistry and improves significantly for charged systems and transition metal chemistry, which we will show for various benchmarks by comparing to highly accurate coupled cluster calculations.



Figure 1: Performance of PBE0-DH-D/def2-QZVPP on the MOR41 transition metal reaction energy benchmark[4].

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Incorporation of radionuclides in green rust

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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.



Iron (Fe) is the fourth most abundant element in the earth crust and it is commonly found to form together with O, and/or OH either oxides, hydroxides, or oxide-hydroxides. Corrosion products of Fe are expected in the near field of nuclear waste disposal sites and serve as a sink for radionuclides. Under such redox conditions Fe(III) oxides are electron acceptors and form 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. These mineral phases are intrinsic and essential parts of biogeochemical cycling of metals and organic carbon and play an important role regarding the mobility, toxicity, and redox transformation of organic and inorganic pollutants, such as radio nuclides.

Fig. 1 : Fe^{II-III} hydroxycarbonate GR(CO_3^{-2}) [[$Fe_4^{II}Fe_2^{III}(OH)_{12}$]²⁺·[$CO_3^{-2} \cdot 3H_2O$]²⁻.

From a theoretical perspective open shell cases such as Fe(II)/Fe(III)] are very difficult to tackle. We present density functional (DFT+U) calculations on pure Fe^{II-III} hydroxycarbonate GR(CO_3^{-2}) [$Fe_4^{II}Fe_2^{III}(OH)_{12}$]²⁺·[$CO_3^{-2} \cdot 3H_2O$]²⁻. 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}). In a second step we studied the incorporation of radionuclides, such as Ln³⁺, An³⁺ and Iodine⁻ into GR(CO_3^{-2}) and compare with available experimental data [1].

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Boron-Boron One-Electron Bond in an Intermediate of the 1,2-Carbaboration of Unactivated Alkenes

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There have been sporadic reports of stable radical anions with a boron-boron σ bond occupied by a single electron.[1, 2] In a DFT study of the radical pathway of the reaction of alkyl halides (CF₃I) with alkenes (CH₃CH=CH₂) with bis-(catecholato)diboron as the boron source, we have identified a radical anion with a single electron located between two boron atoms as an important intermediate (Fig. 1). It is formed from the diboron reagent and an alkyl radical (CH₃CHCH₂CF₃) in the presence of the donor solvent (DMF).[3]



Figure 1: Radical Anion in the 1,2-Carbaboration of Propene. Spin Density (0.02 a.u.)

We have analyzed the complete reaction mechanism of the 1,2-carbaboration of propene with DFT methods (PWPB95-D3//PBE0-D3+COSMO-RS). In the course of the reaction, radical anion 1 undergoes fragmentation of the B-B bond, generating the reaction product and a solvent stabilized boryl radical which regenerates a new radical by halogen atom abstraction from CF_3I .

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Theoretical Study of Rotational Spectra of Chiral Systems

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Lennard-Jones clusters are clusters of rare gas atoms, whose interaction can be desribed through the Lennard-Jones potential. The potential is based on two-body forces. While most of the clusters have a global minimum structure which is highly symmetric with an icosahedral motif structure, there are cluster sizes for which the global minimum structure is chiral [1]. The smallest of these chiral clusters is LJC-17 which consists of 17 atoms [2].

On this poster, rotational energy levels and transition probabilities of LJC-17 are discussed. The rigid rotor approximation is used to calculate energy levels. As the cluster is an asymmetric top, rotational energy levels which are degenerated for symmetric tops split up and additional transitions become possible. While the electric dipole moment is small, the cluster has a much larger electric quadrupole moment. Therefore, both E1 and E2 transitions are discussed. The tunneling barrier between the enantiomers of the cluster is discussed and the effect on the rotational levels is shown.

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Pressure-induced Effects on Self-cleavage Reaction of Ribozyme Catalysis: A Molecular Dynamics Study

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Ribozymes, a very important class of non-coding RNA molecules, catalyze site specific selfcleavage of phosphodiester bonds and play prominent roles in several biological processes such as RNA splicing, the controlling of gene expression, and processing of tRNA. Ribozymes also serve as a potential drug target. Replica exchange molecular dynamics simulations including explicit solvent and ions were utilized to understand pressure induced effect on self-cleavage reaction of a hairpin ribozyme. We find that the compression of the ribozyme leads to an accelerated transesterification reaction, being the self-cleavage step, although the overall process is slowed down in the high-pressure regime[1]. The results reveal that favourable interactions between the reaction site and neighbouring nucleobases are strengthened under pressure, resulting therefore in an accelerated self-cleavage step upon compression. These results suggest that properly engineered ribozymes may also act as piezophilic biocatalysts in addition to their hitherto known properties.

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Fully Automated Quantum-Chemistry-Based Computation of Spin-Spin-Coupled Nuclear Magnetic Resonance Spectra

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We present a composite procedure for the quantum-chemical computation of spin-spin-coupled ¹H NMR spectra for general, flexible molecules in solution. The procedure is based on four main steps, namely an initial conformer/rotamer ensemble (CRE) generation by the fast tight-binding method GFN-xTB[1] and a newly developed search algorithm, computation of the relative free energies and NMR parameters, and solving the spin Hamiltonian. In this way the NMR-specific nuclear permutation problem is solved, and the correct spin symmetries are obtained. Energies, shielding constants, and spin-spin couplings are computed at state-of-the-art DFT levels with continuum solvation.



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Peroxyl Radical Reaction in Water: the Phenol Case

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ABSTRACT. The reaction of phenols with alkylperoxyl radicals is of fundamental importance in oxidation processes and is difficult to investigate in water. The trapping of peroxyl radicals was found to follow different mechanism, depending on the pH. At large pH, SPLET-like mechanism is favoured which consists of acidic dissociation of phenols prior to their reaction with ROO• radicals. At low pH, direct H-atom transfer can take place, in which water seems to be involved as proton relay in the rate-determining steps [1].



This theoretical work is a first approach to answer the question whether a water-mediated mechanism is taking place. The phenol molecule is presented to react with MeOO[•] in water. Density functional calculations are performed with a network of water using 1, 2, and 3 explicit water molecules between the phenol OH group and the radical. From the transition state of the H-transfer, conclusions on the reaction barrier and the kinetics will be drawn.

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Converged Path Integral Simulations of Reactive Molecules down to Ultralow Temperatures at Coupled Cluster Accuracy

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Performing quantum simulations of reactive molecules, H-bonded species and non-covalently bounded complexes at temperatures of a few Kelvin is a challenge due to the high computational cost of these simulations. Indeed, at such ultralow temperatures, a full treatment of nuclear quantum effects (such as zero-point energy and tunelling) is necessary. [1, 2] This is usually done using methods based on the Path Integral (PI) formalism such as Path Integral Molecular Dynamics (PIMD). Unfortunately, at ultralow temperatures, the computational cost of PI methods become prohibitively high. Moreover, the accurate description of reactivity generally requires the use of computationally expensive *ab initio* electronic structure methods. However, interesting experiments such as helium nanodroplet isolation spectroscopy [3, 4] are performed at these ultralow temperatures and would benefit from complementing simulations. Here we report on our recent progress in reaching ultralow temperatures using reactive path integral simulations to study microsolvated or gas phase molecules. We first introduce a set of tools, namely accelerated PIMD using colored noise thermostats (PIGLET [5, 2] and PIQTB [6]) allowing us to reach temperatures of about 1 K and neural network potentials [7] to efficiently treat interactions at the level of essentially converged coupled cluster accuracy (CCSD(T)) [8]. We then present methodological comparisons and molecular insights obtained on a benchmark system: the Zundel cation $(H_5O_2^+)$ in the gas phase. In particular, the benefits and limitations of the PIGLET and PIQTB methods are discussed in addition to demonstrating how our methodology can indeed give insights into molecular structure and nuclear delocalization properties of small molecules down to temperatures of around 1 K at an unprecedented level of accuracy making the ultralow temperature regime now accessible to fully converged path integral simulations.

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High-Dimensional Neural Network Potential for the Copper-Zinc System

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Neural network potentials (NNPs) are a powerful method to study large systems. They offer the accuracy of density functional theory (DFT) at a computational cost similar to that of classical force fields [1, 2]. This enables us to perform large scale Monte Carlo simulations which would not be possible using DFT.

In the center of our investigation is the copper-zinc system, which is not only relevant for its wide range application in form of brass in the metal industry, but also as an important benchmark system for alloys. We train a NNP using the energies and forces of thousands of structures containing copper and zinc in different ratios. The data for the training set is obtained with DFT employing the PBE functional [3]. As a first step we validate the NNP by calculating the accuracy of predicted energies and forces of structures not contained in the training data. The primary goal is then to explore the applicability of NNPs to bulk brass. For the purpose of finding ordered configurations, we analyze the distribution of the copper and zinc atoms on a regular fcc lattice for various zinc contents.

As an example, we present the results for the lowest energy configurations (Fig. 1) for a composition of $Cu_{0.75}Zn_{0.25}$, which agree with previous investigations [4]. Additionally, we are able to reproduce the dependence of the α -brass lattice constant on the zinc content, in good agreement with experiment [5]. Furthermore, the analysis of simulations of the (100) surface of brass shows that zinc atoms accumulate at the outermost layers. Beyond that, we currently expand the analysis to brass clusters and nanoparticles.



- Fig. 1: Lowest energy configurations, which correspond to the bulk phases L1₂, LPS3, DO₂₃ of α -brass for Cu_{0.75}Zn_{0.25} composition, found in a MC simulation employing a NNP.
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What is the aggregate state of super-heavy Copernicium at ambient conditions?

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Copernicium (Cn, Z = 112) is the youngest and heaviest member of Group 12 (Zn, Cd, Hg) of the Periodic Table of Elements. With a half-life of up to 28 seconds, its most stable isotopes are suitable for atom-at-a-time experiments, which were able to shed some light onto its chemical nature. From data collected in five events, it was concluded that Cn exhibits weak metallic interactions with a Gold surface, while its cohesive energy E_{coh} was estimated at 0.4 ± 0.1 eV by direct comparison to Radon ($E_{coh} = 0.20$ eV) and Mercury ($E_{coh} = 0.67$ eV) [1]. This estimate was recently confirmed in our lab by means of relativistic CCSD(T) calculations, employing an incremental scheme to model bulk Cn, which provided $E_{coh} = 0.38 \pm 0.3$ eV [2]. We furthermore established that plane-wave DFT with the PBEsol functional and a tailor-made small-core PAW pseudo-potential affords very reasonable agreement with CCSD(T) for total ($E_{coh} = 0.35$ eV) and relative energies, as well as relativistic effects.

In this contribution, we describe the exploration of the physico-chemical properties of bulk Cn by means of plane-wave DFT in conjunction with thermodynamic integration to compute and compare Gibbs free energies of its condensed phases. The aim is to solve an almost 50-year old puzzle about the aggregate state of Cn at ambient conditions, which due strong relativistic contraction of the 7s valence shell possesses a noble-gas like electronic structure, and has thus been speculated to be a gas at ambient conditions.[3] Our results indicate a low melting point at 370 ± 20 K, while at the same time the free energy of the gaseous phase modeled as an ideal gas is very close. This agrees well with a previous estimate of the boiling point of Cn at 357^{+111}_{-108} K [1], but altogether hints towards Cn being solid at ambient conditions. Concerning the impact of relativistic effects, we find that in good agreement with CCSD(T), a scalar-relativistic treatment of the valence space reduces E_{coh} by 0.05 eV, which translates into a lowering of the melting point by about 10 K. In the non-relativistic limit, E_{coh} dramatically increases to 1.34 eV, raising the melting point by almost 500 K to 840 ± 30 K. This is the largest relativistic shift of a melting point encountered so far, dwarfing the value of 160 K recently reported for Mercury [4].

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Lessons from the spin-polarization/spin-contamination dilemma of transition-metal hyperfine couplings for the construction of new functionals.

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Local hybrid functionals (LH) are a new and promising approach within the density functional framework, defined by its position-dependent admixture of exact exchange, which is governed by a local mixing function (LMF).[1] The increased flexibility was already shown to provide improved performance in the calculation of thermochemical and kinetic data,[2, 3] while ongoing research aims on further validation and development of the LH scheme, e.g. for the calculation of a variety of molecular properties.[4] The calculation of hyperfine coupling constants (HFCCs) in the non-relativistic limit hereof constitutes a promising model, as (i) HFCCs are known to be extremely sensitive to the admixture of exact exchange and may thus strongly benefit from the improved flexibility of LHs and (ii) the calculation of such first order properties provides a quick assessment of the (parameter specific) quality of the simulated electronic structure (since such first order properties are directly accessible via a simple eigenvalue equation).[5, 6] Here, the performance of different density functional approaches, including newly implemented LMFs, is compared in the calculation of metal HFCCs for different 3d transition metal complexes.

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Energies of Molecular Crystals from Many Body Expansion embedded in fully self-consistent Frozen Density

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Molecular crystals are relevant in different research fields such as pharmaceuticals or organic based semiconductor technologies. Of particular interests are the energy difference between different polymorphic structures of molecular crystals. Predicting these small energy differences with quantum chemical methods is an incredibly difficult task [1].

Wave-function based electronic structure methods are a powerful tool for describing intermolecular interactions, but are generally not available for periodic crystal structures. Instead, (dispersion-corrected) DFT is routinely available for periodic crystal structures, but often does not provide the required accuracy. The many-body expansion provides an appealing approach for calculating the lattice energies of molecule crystals by decomposing it into contributions of subsystems such as dimers, trimers, etc. The decomposition into smaller subsystems allows for the use of wave-function based methods to calculate the interaction energies with sufficiently high accuracy [2].

However, the convergence with respect to the subsystem order in the many-body expansion remains a bottleneck, because the contributions of trimers and tetramers can in general not be neglected. Here, we explore the use of quantum-chemical embedding methods to implicitly account for such high-order contributions [3]. Specifically, we employ fully self-consistent frozen-density embedding (DFT-in-DFT) for the monomer, dimer and trimer calculations. We achieve full self-consistency of the electron density by iteratively converging the subsystem densities in so called freeze-and-thaw-cycles. As test cases, we consider two organic compounds (acetylsalicylic acid, oxalyldihydrazide) in different crystal structures.

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Benchmarking non-covalent interactions with vibrational spectroscopy

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Non-covalent interactions can be described by correlated wavefunction or tuned density functional methods and the latter are often validated by the former. Benchmarking against experiment is less popular, because relevant observables such as energy and structure involve zeropoint vibrational energy (ZPVE) contributions which complicate the connection to electronic structure theory. Also, spectroscopic properties such as interaction-induced vibrational frequency shifts include anharmonic contributions which are difficult to model even in moderate size molecules. In Göttingen, we explore different strategies which alleviate such ZPVE and anharmonicity problems for electronic structure benchmarking [1]. ZPVE compensation in intermolecular energy balances is used to benchmark small energy differences [2]. Overtone, hot band, and combination band spectroscopy is applied to test anharmonic corrections [3]. Subtle chirality recognition phenomena [4] with compensating ZPVE effects are studied to unravel the delicate interplay between repulsive and attractive contributions. Blind challenges are organized to identify the most adequate experimental and computational tools [5]. These efforts are coordinated with other experimental benchmarking projects through a new research training group [6].

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Counterintuitive Interligand Angles in the Diaryls $E\{C_6H_3-2,6-(C_6H_2-2,4,6-{}^iPr_3)_2\}_2$ (E = Ge, Sn, or Pb) and Related Species: The Role of London Dispersion Forces

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The straightforward reaction of two equivalents of the lithium salt of the bulky terphenyl ligand Li(OEt₂)C₆H₃-2,6-(C₆H₂-2,4,6-^{*i*}Pr₃)₂, with suspensions of GeCl₂·dioxane, SnCl₂ or PbBr₂ in diethyl ether yield the very crowded σ -bonded diaryl tetrylenes of formula E{C₆H₃-2,6-(C₆H₂-2,4,6-^{*i*}Pr₃)₂} (E = Ge (1), Sn (2), Pb (3)) as blue crystalline solids. Despite their high level of steric congestion, X-ray crystallography showed that compounds 1 - 3 possess C_{*i*pso}-E-C_{*i*pso} interligand bond angles in the range of 107.61 – 112.55° which are narrower than those observed in analogous species with less bulky terphenyl substituents. The relatively narrow interligand angles displayed by 1 - 3 are attributed in part to the increase in London dispersion force interactions between the two Ar^{*i*Pr6} (Ar^{*i*Pr6} = -C₆H₃-2,6-(C₆H₂-2,4,6-^{*i*}Pr₃)₃) groups from carbon atoms in some of the isopropyl substituents and several carbon atoms from the flanking aryl rings. The D3^[11] dispersion corrected density functional theory (DFT) calculations were carried out at the PBE0/def2-QZVP level on the full series of diaryl tetrylenes, E(Ar^{*i*Pr6})₂, E(Ar^{*i*Pr4})₂ (Ar^{*i*Pr4} = -C₆H₃-2,6-(C₆H₃-2,6-^{*i*}Pr₂)₂) and E(Ar^{Me6})₂ (Ar^{Me6} = -C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂, affording attractive dispersion interaction energies as high as *ca*. 27 kcal mol^{-1,[2]}



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Photoassociation processes of Rb₃ and kernel based methods for generating global potential energy surfaces

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Understanding molecular binding mechanisms on a fundamental level and creating molecules in exactly defined quantum states are major goals in the growing area of ultracold chemistry. An important method to produce ultracold molecules is photoassociation which has been demonstrated for Rb dimers in [1]. At the same time an experimental realization of higher associated clusters succeeded so far only with alkali metal atoms formed on helium droplets [2]. An encouraging approach for preparing isolated Rb₃ molecules combines photoassociation with cavity QED allowing for non-destructive detection of ultracold molecules [3].

In order to propose a realistic photoassociation scheme we apply MRCI with a scalar relativistic large core effective core potential and core polarization potential to calculate possible states and transitions for both doublet and quartet states of Rb₃ clusters. However, for an experimental realization of the trimer complex knowledge of the expected lifetimes of states as well as having Franck-Condon factors at hand is inevitable. These properties are directly related with the corresponding potential energy surfaces (PESs). Therefore we apply kernel based methods to construct physically meaningful global PESs with accurate long-range behaviour [4, 5] from *ab-initio* data.



Figure 1: Fitted $(a)^{3}\Sigma_{u}$ potential energy curve of Rb₂ (left) and two-dimensional cut of quartet ground state potential energy surface of Rb₃ (right).

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A Theoretical Study of Gas Hydrates

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Gas hydrates are solid materials, which consist of a water framework with gas molecules (e.g. H_2 , CO_2 , CH_4 and higher organic molecules) contained in its cavities. On the one hand, these compounds are problematic due to the fact that they can plug gas pipelines, on the other hand, they offer the capability of unpressurised gas storage. Quantum chemical calculations have been performed to understand the thermodynamic background of the formation of these gas hydrates, their stability and their storage capacity: The hydrate structures were optimized using the density-functional tight-binding (DFTB) method. Grand canonical Monte Carlo (GCMC) simulations of sI and sII gas hydrates were performed to calculate large and small cage occupancies for given temperature and pressure values. A thermodynamic model for hydrate formers combined with highly accurate equations of state (EoS) in form of the Helmholtz energy for fluid phases and with Gibbs energy models for pure solid phases as implemented in a thermophysical property software named TREND has been used for comparison. To study the dependency of the gas hydrates' lattice constant on the cage occupancy, geometry optimizations using the DFTB method were performed in addition to the GCMC simulations.



Schematic illustration of the (a) sI and (b) sII clathrate structures.

Implementation of the resolution of the identity approximation for complex scaled basis sets.

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Ionization of molecules in intense laser field is a fundamental process observed in many applications, notably, laser-induced electron diffraction [1], imaging of molecular orbitals [2], and in experimental methods for probing nuclear dynamics with attosecond resolution [3].

At low frequencies and high field strength of the electromagnetic radiation, ionization of molecule can be modeled by computation of static-field ionization rates. A convenient option is a non-Hermitian time-independent treatment based on the introduction of complex basis functions [4]. The main idea of this formulation is to transform the divergent resonance wave function into L^2 integrable, allowing the application of standard ab initio bound state methods. The Stark shift and the ionization rates can be directly extracted from the complex eigenvalues of the Hamiltonian. This approach have been implemented recently using the CCSD approximation to study strong-field ionization in small molecules [5, 6]. However the CC formulation is suitable only for small systems.

In this work we introduce the RIMP2 method in a complex scaled basis set with the aim of speeding up calculations and extend the analysis of electronic resonances to larger molecules. Ionization rates and Stark shifts of some molecules in static electric fields are computed in a basis set and auxiliary basis set of atom-centered Gaussian functions with complex-scaled exponent. We compare RIMP2 with CCSD results for simple molecules in order to asses the performance of our approximation.

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Girsanov reweighting for Metadynamics

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Many molecular processes, such as protein-protein interactions or protein-ligand binding events, are not accessible with direct MD simulation. Enhanced sampling techniques, such as metadynamics[1] or umbrella sampling, in which a biasing potential U(x) is added to the unbiased force field V(x) increase the sampling of rare events. However, the distortion of the timescales in the system due to the biasing potential is not uniform. The resulting biased trajectories can hence not be used to estimate models of the molecular dynamics, e.g. Markov state models.

We will present the Girsanov reweighting method[2,3] with which one can estimate the expected path ensemble average of an unbiased dynamics for a set of biased paths. The method is based on the concept of path probability measure and the Girsanov theorem, a result from stochastic analysis to estimate a change of measure of a path ensemble.

Since Markov state models of molecular dynamics can be formulated as a combined phase-space and path ensemble average, the method can be extended to reweight these models by combining it with a reweighting of the Boltzmann distribution.

We will show how Girsanov reweighting can be implemented with metadynamics simulations[4], in order to obtain Markov State Models of the unbiased systems whose dynamics is too slow to efficiently explore its phase space by direct simulation. We will present results for a one-dimensional diffusion process, alanine dipeptide, and the hexapeptide VGVAPG. The results are compared to reference models obtained from unbiased simulations.

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Complex scaling for one-dimensional model systems

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Complex scaling of the Schrödinger equation $(r \rightarrow r \cdot e^{i\theta})$ provides access to resonance states in molecular systems [1]. Resonances are metastable states embedded in a continuum of unbound states. When increasing the rotation angle θ , the continuum states are rotated in the complex plane, while bound as well as resonance states are independent of θ . However, complex scaling methods require the use of large basis sets to recover this expected θ -dependance [2].

Already calculations for small model systems require a large basis set, which makes them infeasible for applying this method to more complicated molecular systems.

Here we investigate the basis set dependance of complex scaling methods for a series of onedimensional model systems. Specifically, we perform complex-scaled calculations for a onedimensional free-particle, particle in a box, a harmonic oscillator and a resonance potential.

We compare the exact solutions and different basis set expansions and their dependance on the scaling parameter θ . We find that the use of a θ -dependent basis set expansion can overcome the basis set requirements of complex scaling methods and recovers the exact θ -dependance already with small basis sets.

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Electronic structure calculation in Electrochemistry -Pt nanoparticles on carbon and electrochemical potential

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High Resolution Transmission Electron Microscopy (HR TEM) is used to identify the size, shape and interface structure of platinum nanoparticles and carbon support of a fuel cell catalyst. Using these insights, models accessible to quantum chemical methods are designed in order to rationalize the observed features. Thus, basal plane and prism face models of the carbon black material are considered, interacting with Pt clusters of sizes up to one nm. Particular attention is paid to the electronic structure of the carbon support, namely the radical character of graphene zig-zag edges. The results show that a stronger interaction is found when the nanoparticle is at the zig-zag edge of a basal plane due to the combination of dispersion interaction with the support structure and covalent interaction with carbon atoms at the edge. In this case, a distortion of both the Pt nanoparticle and the carbon support is observed, which corresponds to the observations from the HR TEM investigation. Furthermore, the analysis of the charge transfer upon interaction and the influence of the potential on the charge states and structure is carried out on our model systems. In all cases, a clear charge transfer is observed from the carbon support to the Pt nanoparticle. We show that changing the potential not only can change the charge state of the system but can also affect the nature of the interaction between Pt nanoparticles and carbon supports. Finally, a discussion is open on the inherent problems in modeling the potential in electrochemistry.



Figure. Black dots: interaction energies between the Pt NPs and the different supports; Red boxes: dispersive contribution to the interaction energy; Blue boxes: covalent contributions to the interaction energy. Horizontal solid and dashed black lines correspond to the minimum Pt-C and Pt-H distances (right y-axis), respectively.

Photomigration in azo-polymer thin films studied by atomistic MD simulations

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Thin films of photoresponsive polymers containing azobenzene (AB) as the photochromic unit are well known for allowing photopatterning and the fabrication of surface relief gratings (SRGs) [1,2]. In this contribution, we present recent results from our theoretical studies based on multiscale molecular dynamics (MD) simulation techniques [3,4] applied to the phenomenon of light-induced mass transport – also being termed photofluidity [5] – in an active layer slab of poly-disperse-orange-3-metacrylamide (PDO3M) [6] exposed to a structured light-field. Explicitly including light-induced isomerisaton dynamics in the $E \rightarrow Z$ as well as the $Z \rightarrow E$ direction, we compare different polarisaton scenarios of the incident light beam in order to elucidate the diverse experimental observations in this field.

This work is supported by DFG (Project DO 768/4-1, Paketantrag "Multilevel-molekulare Assemblate (MMA): Struktur, Dynamik und Funktion (PAK 943)").

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Study of a molecular torsion balance in solution

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The Wilcox torsion balance represents a prototype system of a large molecule that possesses a comparably simple conformational energy landscape [1]. Namely, the two predominant conformer structures are of the folded type, characterised both by stabilising CH-pi and sigmastacking interactions of the terminal alkyl chains, and the corresponding unfolded conformation. Recently, Yang et al. [2] have measured the free energy of folding in various solvent environments and found the results to be one order of magnitude smaller than those obtained by corresponding dispersion-corrected DFT calculations performed in the gas-phase. This indicates a strong impact of the solute-solvent interaction in the system which compete with the intramolecular interactions. In this study, molecular dynamics simulations combined with the MD-quench technique have been performed in order to sample the conformational landscape of the molecule in various solvent environments and for extracting local minima on the potential energy surface. These structures have then been studied with high-level DFT and DFT-SAPT methods [3] combined with our incremental molecular fragmentation method [4] in order to estimate the magnitudes of the inter- and intramolecular interactions. It is shown that, almost irrespective of the polarity of the solvent, the energy gain due to the folding is almost completely quenched by the reduction of the interaction with the solvent molecules. The mechanism of the folding in solution can therefore be qualitatively explained even without taking into account entropic contributions like the solvophobic effect.

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Eletronic g-tensors with density functional theory: study of the gauge-origin dependendence and sub-linear scaling implementation

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We present a benchmark study on the gauge-origin dependence in electronic g-tensor calculations. The used density functional theory method employs the spin-orbit mean field operator for the spin-orbit coupling effects. The reference values are obtained from an implemented ansatz that uses gauge-including atomic orbitals (GIAOs) and provides gauge-origin-independent results; the obtained values are compared to values computed with common gauge-origin approaches that suffer from gauge-origin dependence. Furthermore, the errors introduced through gauge-origin dependence are compared to the basis set error. The results indicate that common gauge-origin approaches are only reliable for very small molecules; for larger systems significant errors can be introduced. A new pragmatic ansatz for choosing the gauge-origin is proposed which takes the spin density distribution into account and gives reasonably accurate values for molecules with a single localized spin center; it is shown to be superior to the commonly employed electronic charge centroid as gauge-origin. For large systems with less local spin density distributions only distributed gauge-origin approaches like the GIAO method provide reliable g-tensors.[1]

Furthermore, an efficient implementation of the GIAO ansatz with the spin-orbit mean field operator is presented. Asymptotically linear scaling with molecule size is achieved with integral screening methods and sparse linear algebra. In addition, we introduce ansätze that exploit the locality of the contributions to the g-tensor for molecules with local spin density by restricting the coupled-perturbed self-consistent field equations to the relevant orbital space. For such systems sub-linear scaling is achieved. The presented method enables efficient, accurate and gauge-origin independent computations of electronic g-tensors of large molecular systems.

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DFT study on the thermodynamics and kinetics of a novel organocatalysed fivestep one-pot synthesis

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Mechanism of the novel organocatalysed five-step one-pot process [1]

Phenylacetaldehyde 1a, malononitrile 2a and trans- β -nitrostyrene 11 react in an organocatalyzed five-step one-pot process to a novel substituted o-terphenyl 14 via a potentially bioactive intermediate 9a [1]. We carried out a density-functional study on the involved reaction steps to shed light on the thermodynamics of all involved reactions as well as the kinetics of the vinylogous Michael addition [2]. From these calculations we deduce, that the SR enantiomer of intermediate 9a (SR-9a) is formed with a reaction Gibbs free energy of -7.1 kcal/mol, while the RR enantiomer of 9a (RR-9a) is formed with a reaction Gibbs free energy of -6.1 kcal/mol. Subsequently the o-terphenyl 14 is formed with a reaction Gibbs free energy of -74.7/75.7 kcal/mol, respectively. Our DFT study on the kinetics revealed, that the formation of the RR-enantiomer of 9a is kinetically favored by ~ 1 kcal/mol. Overall the formation of SR-9a is thermodynamically favored while the formation of RR-9a is kinetically favored. Furthermore, we studied the influence of dispersion interactions.

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Computational Design of NHC-based Molecular Ratchets

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N-Heterocyclic carbenes (NHCs) have received much attention for their many uses, including the modification and stabilization of surfaces and nanoparticles [1]. In particular, their strong binding to gold surfaces has been shown to be tunable by the choice of N-substituents [2].

In here, the functionality of NHCs as molecular ratchets — specifically, unidirectional rotors on metal surfaces — is explored by computational models spanning multiple length and time scales. Molecular Dynamics (MD) simulations of specially designed, chiral NHCs employing reactive force fields elucidate the interaction of N-substituents with the surface, revealing a tunable sawtooth-like rotational barrier. Density Functional Theory calculations are then used to produce Scanning Tunneling Microscopy (STM) images of rotating NHCs, reproducing experimental results.

Furthermore, we explore the possibility to induce the necessary non-equilibrium dynamics that can drive the ratchet in one direction by electron transfer from an STM tip to the NHC. For this purpose, we have developed a method to control electron transfer processes within the framework of Car-Parrinello MD simulations by restraining the dynamics of maximally localized Wannier orbitals. This way, theoretical methods ranging from classical treatment of atoms to fine control of single electrons are combined to pave the way for understanding and designing NHC-based molecular ratchets.



Figure 1: Schematic of the unidirectional ratchet-like rotation of an NHC on a gold(111) surface.

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GFN2-xTB: An extended Tight-Binding Quantum Chemical Method for Structures, Frequencies and Noncovalent Interactions across the Periodic Table

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A new semiempirical tight-binding model is presented, which is the successor to the previously developed GFN-xTB.[1] The essential novelty in this GFN2-xTB scheme is the inclusion of anisotropic second order density fluctuation effects via cumulative atomic multipole moments and the usage of the D4 dispersion model. Without a significant increase in the computational demands, this results in a less empirical and overall more physically based method, which does not require any additional halogen or hydrogen bonding corrections. The GFN2-xTB method performs overall excellent for the desired "target" poperties including geometry optimizations, vibrational frequency calculations and noncovalent interactions. It often shows even lower errors for "off-target" properties such as reaction barrier heights and molecular dipole moments. This reflects the less empirical nature and the overall improved physics of the GFN2-xTB method, which exclusively relies on element-specific and global parameters. As with the GFN-xTB [1], all elements up to radon (Z = 86) are currently covered.



Figure 1: GFN2-xTB, a semiempirical tight-binding method for geometry optimizations, vibrational frequencies and noncovalent interactions.

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Benchmark and Application of LC-DFTB on the Fenna-Matthews-Olson Complex

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LC-DFTB [1][2] is a promising method for the study of excited state properties of light harvesting systems. Due to the long-range (LC) correction implemented in the efficient DFTB method, extended geometry sampling of chromophores can be combined with relative accurate subsequent calculations. We present a benchmark study of LC-DFTB discussing geometrical and environmental effects on the excitation energies of Bacteriochlorophyll a compared to conventional methods, especially the ZINDO/S-CIS method. We investigated chromophore structures obtained by optimization with different methods and by sampling with classical molecular dynamics simulations as well as QM/MM simulations. The Fenna-Matthews-Olson complex serves as biological test system.

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Complex Formation Trends of Ligand Binding toward In³⁺ and Ge⁴⁺

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In recent years, the demand for strategic elements such as Indium and Germanium has increased due to strong global economic growth, especially in the realm of semiconductors. Dwindling resources and growing demand necessitate new recycling strategies and the reassessment of existing repositories in the light of newly developed technologies. In this context, QSAR methods can be utilized in the development of chelating ligands designed for high affinity toward strategic elements. Through this, novel ligand concepts can be rapidly assessed and synthesis can be prioritized toward promising ligands, resulting in a shortened development cycle and reduced research costs.

In our quantum chemical study, we analyze a systematic set of chelators with respect to their complex formation energies toward selected In^{3+} and Ge^{4+} complexes. Following a first principles approach, both Density Functional Theory and higher levels of theory have been used for the calculations, also addressing bulk solvation effects. The study focuses on both affinity and selectivity. General trends in binding affinity to selected ions are discussed as related to the electronic structure of the compounds. Chelator selectivity toward In^{3+} and Ge^{4+} is investigated in comparison to Fe^{3+} , Cu^{2+} and Zn^{2+} . The importance of both properties arises from expected high concentrations of these interfering ions relative to the strategic elements of interest.

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Geometry Optimizations in a Subsystem DFT Formalism - A Structural Benchmark Study

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Subsystem DFT (sDFT), a subsystem approach to density functional theory which uses Frozen Density Embedding (FDE), is an efficient alternative to Kohn-Sham density functional theory (KS-DFT) for complex chemical systems [1–5]. By partitioning the total electron density $\rho_{tot}(\mathbf{r})$ into a set of smaller subsystem densities, the ansatz introduces a favorable scaling with the number of subsystems.



Fig. 1: Overall performance on the A24 test set.



Fig. 2: Structure optimization with halogen bonding in trichloroacetic acid tetramer.

Here, we present a structural benchmark of sDFT geometries using the analytical sDFT gradient implementation in SERENTY [6]. Since the method is inherently well suited for the calculation of weakly interacting systems, the S22 and A24 test sets serve as references. The three most commonly used functional combinations in the context of sDFT (LDA/TF, PW91/PW91k and BP86/LLP91 + D3(BJ)) are tested thoroughly, with the intent of challenging the previously used strategy to rely on error cancellation effects between exchange-correlation and nonadditive kinetic-energy approximations for medium-range dispersion as is typical for PW91/PW91k [7]. The results show that structures obtained with BP86/LLP91 including explicit D3(BJ) dispersion correction are superior to their LDA/TF and PW91/PW91k counterparts [8].

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Effect of Non-covalent Interactions on the Fluorescence Quenching Mechanism of Polymeric Sensors with Nitroaromatic Explosives

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Silafluorene- and silole-containing polymers are promising materials to be used as chemical sensors for explosives detection. In this study, their binding mechanisms with explosive and non-explosive materials have been differentiated by comparing the relative stabilities of their complexes [1]. The electron density topology was analyzed using the quantum theory of atoms in molecules (QTAIM) methodology to understand the nature of the non-covalent interactions that are responsible for analyte-polymer binding. The carbon and germanium analogues of silafluorene-containing dimers are modeled with the same methodology for a better understanding of the role of silicon in these polymeric systems.

The optoelectronic properties of these polymers as well as their constituent units have been investigated by modeling the properties of their excited states using TDDFT [2].



Figure 1. Alternative Binding Modes of Model Oligomer with TNT

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UV Absorption and Magnetic Circular Dichroism Spectra for Purinic Nucleobases in Aqueous Solution at COSMO-RI-CC2

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We developed the COSMO-RI-CC2[1, 2] theory within the post-SCF[3] scheme in Turbomole program package in order to calculate bulk solvent effect on vertical electronic excitation energies, oscillator strengths and Faraday \mathcal{B} terms. As the first application, the absorption and magnetic circular dichroism (MCD) spectra of three purinic nucleobases: purine, adenine and guanine, were computed at COSMO-RI-CC2 level in aqueous solution to estimate the influence of isotropic environment on transition energies and the relative positions of $\pi\pi^*$ and $n\pi^*$ states of these nucleobases. In the case of adenine, the hydration effect via adding explicit water molecules was also investigated along with the implicit COSMO solvent model in order to figure out how significant is the influence of the anisotropic environment on the absorption spectra comparing to the isotropic one(Fig. 1).



Figure 1: The UV absorption and MCD spectra for adenine with and without water cluster in vacuo and in aqueous solution modeled by COSMO at RI-CC2/aug-cc-pVTZ level. (ε =80.4 and n²=1.78)

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Efficient calculation of Raman spectra and excitation profiles with real-time propagation

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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 perturbation theory TDDFT (PT-TDDFT), like Sternheimer's or Casida's approach, a direct numerical integration of the time dependent Kohn-Sham equations (TDKS) is also viable for the calculation of spectroscopic properties [1]. Distinct features of this real time TDDFT (RT-TDDFT) approach are an advantageous scaling for larger systems, a non-perturbative treatment of electro-magnetic fields and the complete spectral range from just one simulation run.

Two short time approximations (STA) for the calculation of Raman spectra have been applied in a RT-TDDFT framework: The RT polarizability method and the excited state gradient method, which has been possible due to a sufficient resolution in the frequency domain by the use of Pade approximants. Taking advantage of characteristics of RT-TDDFT, non resonance and resonance Raman spectra are calculated at once and compared to their PT-TDDFT counterparts. Thus an automated procedure to obtain entire excitation profiles was created. This approach will be very valuable for the spectroscopic investigation of functional systems, in particular for light-driven processes.

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Molecular Dynamics Simulations of Ionic Liquid Based Electrolytes for Na-Ion Batteries: Effects of Force Field

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Over the past years scientists have focused their efforts in order to develop efficient energy storage technologies with rechargeable lithium batteries being one of the most successful devices of such a type. Unfortunately lithium is not regarded as a very abundant element, which in addition of the constant increase in demand for storage devices stimulates scientists to consider other options.

One of the most promising alternatives for lithium-based batteries are those based on sodium and containing solutions of its salts in room temperature ionic liquids. Apart from the high availability of sodium at low prices all over the world, sodium batteries have excellent electrochemical features.

In our research[1] we tested the performance of MD simulations in modeling of Na⁺/ionic liquid electrolytes (NaTFSI/EMIM-TFSI with increasing Na⁺ concentration) for which experimental data became available recently[2]. We used several non- and polarizable classical force fields to check the quality of reproduction of experimental data at reasonable computational cost. Structural properties of electrolytes (radial distribution functions or conformations of anions) were analyzed. MD trajectories up to 1 μ s long were used to calculate viscosities and ion transport properties (diffusion coefficients and conductivities).

Results obtained within different parametrizations and their agreement with measured values significantly depend on the type of force field. Predictions of nonpolarizable calculations generally agree with available experimental data and reproduce trends observed in electrolytes with increasing salt content. Nevertheless, some trends were better reproduced in polarizable simulations suggesting that such FFs are worth investing effort in improving the parametrization.

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Development of a relativistic diabatic potential model for the treatment of the nonadiabatic photodissociation of iodobenzene

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The photodissociation of iodobenzene (PhI) is a process of fundamental interest, since it allows for detailed insights into the dynamics of nonadiabatic reactive processes. The system features not only multiple state crossings but also relevant spin-orbit coupling. While this has been studied extensively on the example of CH_3I as a benchmark system, PhI is much more complex, even with no accounting for spin-orbit coupling. While CH_3I only shows spin-orbit induced conical intersections, PhI has a much higher density of electronic states causing vibronic state interactions in addition to spin-orbit coupling. The goal of the present project is the development of a fully coupled diabatic potential surface (PES) model for quantum dynamics treatment of the photodissociation process.

The method we use to account for spin-orbit coupling is the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) approach recently developed by us [1]. In this method, the molecule is split into fragments (I and C_6H_5) so the relativistic coupling effects can be treated entirely within the framework of atomic iodine. This way, the effective relativistic coupling can be described by a constant spin-orbit coupling matrix and the geometry dependence is accounted for by the diabatization.

A large number of singulet and triplet electronic states of PhI have been computed and analysed along the dissociation coordinate. These data were obtained by CASSCF and MRCIcalculations. The data shows that mostly the first 6 singlet and triplet adiabatic states are relevant for the nondiabatic photodissociation processes and most of them are dissociative. As expected, most of these states show conical intersections or avoided crossings along the dissociation coordinate. Singlet and triplet states are also interacting through the spin-orbit operator. The present data allows for the setup of the ERCAR model which will be presented.

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Automated Computation of Nuclear Magnetic Resonance Spectra

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Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most important analytical technique in chemistry providing thermodynamic and structural insight. So far, the automated calculation of NMR spectra has been problematic due to the NMR-specific nuclear permutation problem. A routinely applicable, fully automated scheme for quantum chemical calculation of ¹H-NMR spectra was recently presented [1]. The approach heavily relies on the generation of the correct conformer/rotamer ensemble (CRE). It is calculated with a procedure based on normal mode following, molecular dynamics, and genetic structure crossing algorithms using the robust semiempirical Geometry, Frequency, Noncovalent, eXtended Tight Binding (GFN-xTB) method [2].

In this work, several ¹H-NMR spectra of organic molecules (~50–150 atoms) in solution are calculated and compared with experimental spectra. The influence of implicit solvation models, the new GFN2-xTB method [3], as well as new density functionals (including double hybrids) for computing shielding constants are investigated.



- Figure 1: Calculated (black) and experimental [4] (grey, inverted) NMR spectrum of L-DOPA in water.
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Extension of the element parameter set for ultra fast excitation spectra calculation (sTDA-xTB)

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The extension of the parameter set for an ultra-fast electronic excitation spectra calculation is presented. The semiempirical theory based on a tight-binding approach, called extended tightbinding (xTB) in combination with the simplified Tamm-Dancoff approximation (sTDA)[1] shows remarkable accuracy at very low computational cost for the calculation of vertical excitation energies of molecules. It enables the possibility for computing even large systems up to thousands of atoms or sampling along molecular dynamic (MD) trajectories. The original publication of the sTDA-xTB[1] method included parameters for the most important elements (H-Zn,Br,I). In this work, element parameters for 4d and 5d metals, and the missing ones in 4p, 5p and 6p element blocks are presented and analyzed for their quality. Comparisons to theory and experiment show that sTDA-xTB provides similar good results as for the elements in the original publication with an average deviation of excitation energies of 0.3–0.5 eV.

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Optimization of phosporescent Platinum(II) complexes on solid substrates

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Luminescent organometallic complexes are the subject of intense current research due to their application in low-cost, printable optoelectronic devices such as organic light emitting diodes (OLED). Density functional theory based electronic structure calculations and molecular dynamics simulations are used here to predict the photophysical properties and stability of different tetradentate Platinum(II) complexes. In addition to the isolated species, a particular focus is on their interaction with the environment, hence they are also studied in aggregates, in solution, and on solid surfaces. To enable the complementary experimental characterization of the Pt-complexes by scanneling tunneling microscopy (STM), one of our aims is to design complexes that exhibit a high degree of planarity and stability on metal (e.g. Au, Ag, Cu) surfaces.

STM images of a tetradentate Pt-complex with two difluorobenzene ligands and a pyrimidine head group (see Fig. 1) evaporated onto a Cu(111) surface suggest that the head group is catalytically removed on the surface leaving behind a planar product. In this work, we investigate the possible underlying chemical reaction mechanism together with the corresponding electronic structure analysis and energetics along the reaction path (see Fig. 1). The strong interaction between the absorbate and the surface is rationalized in terms of the molecular orbitals involved.



Figure 1: Optimized geometries of the tetradentate Pt complex on Cu(111) at different distances along the C-N dissociation coordinate (left: 1.4 Å and right: 3.4 Å).

Benchmarking of Machine Learning algorithms in the context of constructing potential energy surfaces

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Algorithms originating in the field of machine learning (ML) gained a lot of interest in the recent years and found its way into Quantum Chemistry as shown by recent work from different groups as indicated in a recent special topic[1] in the Journal of Chemical Physics.

In this work we want to asses different ML algorithms in the context of constructing potential energy surfaces (PESs). We apply various types of Gaussian Process Regression (GPR), Kernel Ridge Regression (KRR), support vector regression (SVR) and neural networks (NNs) to predict the molecular energy based on information usually gathered to construct a PES in order to get a broader overview of available computational methods with its strengthes and weaknesses.

For constructing PESs we apply the *n*-mode expansion[2] and use the data gathered on the n-1 level to train the ML algorithm. In combination with delta learning the errors in fundamental frequencies are for a PES including 3 mode couplings below 1 cm⁻¹ and therefore smaller than error introduced by other approximations like missing relativistic or higher order correlation effects.



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Interparticle Coulombic decay in paired quantum dots: Exact two-electron dynamics vs. one-electron dynamics on coupled effective potentials

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Semiconductor quantum dots (QDs) are important building blocks of nanometer-sized optoelectronic devices. Charge carriers in QDs are subject to quantum-confinement, resulting in a discrete atom-like electronic structure. Various fabrication techniques allow to tailor the quantum-confinement and thus the optical properties of QDs. In view that QDs can be arranged in pairs, clusters and arrays, it is important to investigate and understand inter-QD energy-transfer processes. The interparticle Coulombic decay (ICD) [1, 2] is an ultra-fast and ubiquitous energy-transfer process, whereby an excited atom, molecule or QD electron relaxes through the ionization of a neighboring atom, molecule or QD, see Figure 1. ICD in paired QDs has accurately been described in a model based on the conduction-band effective-mass approximation, employing a properly antisymmetrized two-electron wave function, for which the TDSE is solved within the framework of MCTDH [3, 4]. Since for large inter-QD distances the exchange part of the el.-el. interaction becomes negligible, the ICD dynamics may approximately be described via the dynamics of one electron in the ionized QD, while the two states of the relaxing QD are described by effective potentials. The coupling between the two states is expressed via transition Coulomb-interaction matrix elements. The ICD rates and the directionality of the leaving electron obtained from the effective single electron dynamics were found to compare well to accurate results from two-electron dynamics for a variety of paired QD geometries. In the future, we want to apply the method to paired metal-nanoparticle - QD systems.



Figure 1: Left: Sketch of ICD process in paired QDs. Right: Decay widths from exact two-electron dynamics and from one-electron dynamics on two coupled effective potentials.

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Ab initio computation of Förster resonance energy transfer

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Enhancing the light-harvesting capabilities of different MTPP (M=Zn, Cu, Pt) linked to a BOD-IPY dye by a triazole-bridge via Förster-Resonance-Energy-Transfer (FRET) were investigated utilizing a dimer-centered basis set (DCBS) and transition densities obtained from the Bethe-Salpeter equation [1]. The zinc-species was previously investigated by Dinolfo *et al.* and deemed to be a good candidate as a light-harvesting device [2]. The close proximity of both subsystems prohibits the use of the Ideal Dipole Approximation (IDA), which is neither an upper nor lower limit for the resulting complete expression involving the full Coulomb potential. The usage of the Resolution-of-the-Identity (RI) approximation appears to introduce no significant error if MP2 fitting basis sets (CBAS in TURBOMOLE jargon) are used and leads to significant improvements in efficiency.



Figure 1: Metalloporphyrin with BODIPY linked via a triazole-bridge.

Strong couplings seem to occur for a variety of states in all systems. The expected coupling from BODIPY S1 to the energetically low lying characteristic Q-bands of the porphyrin appear to be weaker compared to higher excitations.

A generalization of the theory to a two-component description of the systems involving relativistic corrections in the calculation of the transition densities was implemented using the RI-approximation and tested for several small test molecules.

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A new DFT Approach to Spin Densities and Exchange Coupling Constants for Polyradical Systems

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Modeling of macroscopic magnetism only from a solid-state structure is an error-prone task. Our group has recently developed a black-box approach [1] which is based on the so-called first-principles bottom-up approach [2] and qualitatively predicts and analyses the relation between a crystal structure and its magnetic properties. This method uses broken-symmetry (BS) Kohn–Sham density functional theory (KS-DFT) calculations for the prediction of magnetic coupling constants and was applied to various verdazyl radicals [1, 3, 4].



However, approximate KS-DFT has problems in describing polyradical systems due to the effects of the self-interaction error. Subsystem DFT (sDFT) is computationally less demanding than KS-DFT and allows to predefine the spin state for each subsystem. We demonstrate that sDFT is able to converge to BS-like states, even in cases where KS-DFT fails. We also illustrate that spin densities and exchange coupling constants calculated with sDFT are more robust than the ones obtained with BS KS-DFT, although the coupling constants appear to be systematically smaller. Therefore, we investigate the influence of the non-additive exact exchange on the calculated coupling constants and discuss how this can be included in sDFT calculations.

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Exciton coupling in chlorophyll-lutein heterodimer of LHCII photoantenna is significantly affected by the size of MCSCF space for lutein calculation

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Non-photochemical quenching (NPQ) of chlorophyll fluorescence is a fast response mechanism developed by photosynthetic organisms to protect them from excessive light illumination which can lead to irreversible damage of photosynthetic apparatus. Excitation energy transfer from a pool of chlorophylls *a* to lutein molecule is supposed to be the main pathway of NPQ in LHCII complex. More precisely, energy transfer rate from the S_1 state of the closest chlorophyll to the S_1 state of lutein governs rate of NPQ, and is proportional to the squared exciton coupling between them according to Fermi's golden rule. Optically dark S_1 state of lutein ($2A_g^-$ state if one assumes ideal polyene symmetry for lutein) has strong multireference character, and requires large active spaces in MCSCF to account for static correlation.

We studied an impact of active space size in MCSCF calculations on exciton coupling in the aforementioned pigment pair. Ground state geometries for both pigments were optimized in *vacuo* at B3LYP/6-31G* level, dipole moment and transition density for S_0 -> S_1 transition were obtained using MCSCF (in CASSCF and RASSCF formulations). π -orbitals in active space were prepared by projecting orbitals from minimal ANO-MB basis set to ANO-VDZP which was used for final calculation. For CASSCF, active spaces from (4,4) to (14,14) were examined; for RASSCF, two sets were examined: from (20,1,1;8,4,8) to (20,1,1;5,10,5) and (20,2,2;8,4,8) to (20,2,2;6,8,6), where notation (N_{el}, N_{orb}) was used for CASSCF and $(N_{el}, N_{hole}(RAS1))$, Nel(RAS3), Norb(RAS1), Norb(RAS2), Norb(RAS3)) for RASSCF. Averaging with equal weights was performed for 4 lowest states. Additionally, DMRG(20,20)[256] calculation was performed to estimate "full CI" limit of active space containing all π orbitals. S₁ state of chlorophyll a was calculated using RASSCF(20,2,2;8,4,8) to be consistent with results for lutein. Transition densities calculated as described were used to derive effective charges for transition electrostatic potential (TrESP-charges). In order to evaluate exciton coupling, charges were placed on MMoptimized structure of LHCII complex and Coulomb interactions were calculated between them. We have found significant dependence of transition dipole of lutein and, consequently, exciton coupling on active space: dipole varies from 0.40 D for CAS(6,6) (smallest active space predicting correct relative position of $2A_g^-$ state) to 0.060 D for RASSCF(20,1,1;5,10,5). Therefore, due to quadratic energy transfer rate dependence on exciton coupling, calculations in large active spaces are crucial for obtaining correct NPQ rates.

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Excited states with second order approximate internally-contracted multireference coupled-cluster linear response theory

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Based on previous work from e.g. Banerjee and Simmons [1], Hanauer and Köhn [2] have introduced the internally-contracted multireference coupled-cluster theory, namely the singlesand-doubles method with and without pertubative triples (ic-MRCCSD(T) and ic-MRCCSD) as multireference analoga to the well known single reference CCSD(T) and CCSD methods. The new methods are able to accurately consider strong static correlation while improving upon the treatment of dynamic correlation over standard multireference methods like MRCISD. Yet they share the steep scaling in computational cost with their single reference analoga, ic-MRCCSD scales $O(N^6)$ iteratively and ic-MRCCSD(T) includes an $O(N^7)$ non-iterative step. We present a cheaper $O(N^5)$ second order approximate internally-contracted multireference coupled-cluster theory (ic-MRCC2) which can be used to obtain excitation energies in the framework of linear response theory (compare also [3]).

We will present vertical excitation energies for a benchmark set of molecules and compare them to CASPT2, NEVPT2 and full ic-MRCCSD results.

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Diffusion in ionic liquids –alcohol solutions

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To answer a question of a possibility of use of ionic liquids as extracts it is necessary to analyze mechanisms of interaction of ionic liquid with alcohol. The MD was applied using a DL_POLY_4.05. Analysis of the data allowed to establish: (1) The salvation effect in systems ionic-liquid (dmim⁺/Cl⁻) - alcohols solute molecules (methanol, ethanol, propanol and butanol) have qualitatively similar to the behavior of water molecules in IL. The results of the computer experiment for $\langle Etot \rangle$ for the dmim+/Cl– alcohols solutions at T = 400 K show that the intermolecular interaction $\langle Etot \rangle$ does depend on the physical characteristics of dissolved substances. In this case, need to do analysis also of its dynamic properties. Based on the data obtained from MSD and VAF the different diffusion mechanisms of alcohol molecules in IL ware determined.

Multi-dimensional Femtosecond-laser induced dynamics of CO on metals: accounting for electronic friction and surface motion with combined models

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Understanding how adsorbates bind to and behave on metal substrates is crucial for advancements in heterogenous catalysis. Ultrashort laser pulses open up new ways to investigate such systems and may also allow for future applications within the new field of femtochemistry.

We employ two potential energy surfaces, that were recently developed for the well-known model systems CO on Ru(0001)[1] and CO on Cu(100)[2], to simulate hot-electron driven dynamics induced by femtosecond-laser irradiation. The potentials account for all six molecular degrees of freedom of the molecule. Furthermore, surface phonons are also included via the Generalized Langevin Oscillator (GLO) model. Finally, to allow for the coupling of the molecule to electron-hole pairs, electronic friction coefficients derived from the Local Density Friction Approximation (LDFA) are employed in a Langevin approach. There, the action of the ultrashort laser pulses enters through random forces acting on the molecule, which depend on a time-resolved electronic temperature T_{el} , derived from a Two-Temperature Model (2TM). The model is applied to laser-induced lateral diffusion of CO on the surfaces, "hot adsorbate" formation, and laser-induced desorption[3]. Furthermore, for CO on Cu a vibrational analysis was performed to compare with recent time-resolved Sum Frequency Generation (SFG) experiments[4]. Our effectively parameter-free simulations allow for good statistics and treatment of long-time dynamics, giving generally good agreement with experimental data where

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available and detailed mechanistic insight in addition.

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Chemically Accurate Energy Calculation for Molecule-Surface Interactions

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A hybrid high-level QM: low-level QM method is proposed to overcome the typical dilemma in computational material's chemistry between the system size we need to consider and the accuracy we aim. The implemented hybrid QM:QM scheme combines MP2 calculations on a representative cluster model of the active site with DFT+D2 calculations on the entire periodic system. The hybrid MP2:(DFT+D2) potential energy surface (PES) is counterpoise corrected (CPC) for the basis set superposition error (BSSE) and extrapolated to the complete basis set (CBS) limit, as available in the MonaLisa code.[1] *A posteriori*, coupled-cluster CCSD(T) correlation effects are estimated as [CCSD(T) – MP2] energy difference for smaller cluster models and basis sets.

The proposed computational strategy is applied to experimentally well-known adsorption and reaction steps from the field of heterogeneous catalysis: (i) adsorption of methane and ethane monolayers on the MgO(001) surface,[2] (ii) adsorption of small alkanes in the H-chabazite (H-CHA) zeolite,[3] and (iii) methylation reactions via methanol of small alkenes in the H-ZSM-5 zeolite catalyst.[4] It is shown that for the investigated processes - whose models contain several hundred up to thousand atoms - chemical accuracy (± 4 kJ/mol) is reached with respect to experiments and benchmark data are provided with a relatively small computational expense. Within this approach, reference adsorption/reaction energies and structures can be predicted for well-defined coverages and active sites of a catalyst, for which experiments are either not available or they vary significantly due to the complexity of the real catalyst, see e.g. the adsorption study of small alcohols in H-ZSM-5.[5]

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The Tkatchenko-Scheffler and Many-Body Dispersion Methods: Implementation, Validation and Reproducibility in Electronic Structure Codes

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Van der Waals (vdW) dispersion interactions are crucial for the structure, stability, and dynamics of molecules and materials. Thus, these ubiquitous interactions have to be described accurately by means of practical computational methods. In general, vdW interactions are treated by effective non-local methods which then are combined with semi-local and hybrid density functionals. Such a combination enables accurate and feasible calculations of the properties of a wide range of biomolecules, chemical compounds, and materials. In particular, the Tkatchenko-Scheffler (TS) [1] and the many-body dispersion (MBD) [2, 3] methods have been shown to yield excellent results for vdW energy and force contributions in a broad spectrum of systems. Since vdW interactions are rather subtle, one particular problem is ensuring the reliability and reproducibility of vdW implementations in different electronic structure codes. With this goal in mind, we carry out a comparative assessment of the TS and MBD implementations in the codes FHI-aims, Quantum Espresso, and Q-Chem. By choosing codes based on intrinsically different approaches to density-functional theory, our tests cover a wide range of different fields of atomistic modeling. For well-know test sets, ranging from small molecular dimers (S66) to periodic systems (X23), we have calculated binding energies, atomic forces, and relaxed geometries using the different codes. For either vdW method, we found the calculated properties in excellent agreement between the codes (e.g. within 0.1 kcal/mol for binding energies). With our results, we demonstrate the reliability of the implementations of TS and MBD methods in FHI-aims, Quantum Espresso, and Q-Chem [4].

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vdW-TSSCDS: An automated procedure for the computation of stationary points on intermolecular potential energy surfaces

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Characterisation of the topography of Potential Energy Surfaces (PESs) is a tedious task and for large dimensional systems not an evident one. Recently, an automatic methodology (TSS-CDS) for the automatic determination of the stationary points on a PES was proposed by one of the authors [1]. Given a chemically bound molecular system, this methodology relies on a comprehensive sampling of the PES using direct dynamics (semiempirical) simulations and a graph-theory based algorithm to provide transition state guess structures, which are subsequently optimized at an appropriate higher level of theory. A relevant concept in this algorithm is the definition of an adjacency matrix, a square symmetric matrix of dimension of the number of atoms, whose elements indicate whether the corresponding atoms are bound or not. This character, in turn, depends on the definition of a set of covalent radii values.

We have generalized the TSSCDS methodology to study van der Waals and more generally noncovalently bound complexes (vdW-TSSCDS) [2]. Considering such a complex as composed by two well-identifiable fragments, the key idea is the redefinition of the adjacency matrix in a block structure. In this picture, diagonal blocks correspond to the isolated fragments and off-diagonal blocks provide the intermolecular connectivity. To this end, we introduce a new definition of bound or not in a van der Waals sense, by utilizing an extra set of van der Waals distances to determine the elements in the off-diagonal blocks. Additionally, instead of the widely employed rigid approach to the study of intermolecular PES, we have relaxed this condition by adopting a semi-rigid approach in which one of the fragments remains fixed at its equilibrium geometry whereas the other is fully flexible. This gives us the opportunity to study the influence of a substrate on the spectroscopy and reactivity of an adsorbed molecule.

We here present the application to test systems, showing that vdW-TSSCDS does lead to the correct ab initio topography even in limiting cases such as extremely flat regions of the surfaces or non-trivial topologies such as in the case of bifurcation points.

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Isotropic sampling for the accurate representation of bound potential energy surfaces

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The development of potential energy surfaces (PESs) is key for understanding quantum dynamical processes. Typically, the construction of PESs is based on calculating time-consuming *ab-initio* data to be used in interpolation or fitting schemes. As the number of atoms in a system increases, properly sampling all degrees of freedom quickly becomes unfeasible leading to the well-known under-sampling problem. Sampling techniques developed for reactive processes may not yield a good representation of the nuclear configuration space relevant for the quantum dynamics treatment of short-time processes or vibrational dynamics that typically begin in the vicinity of an equilibrium configuration. In addition to this, instabilities in the electronic structure computations may require to use a continuous way of sampling for analysing purposes. In the present study, we propose a novel method to generate an ideal sampling scheme to find the best possible representation of the nuclear configuration space needed to describe short-time and bound state problems. First, a set of random directions starting at a reference geometry is created. This set is then used in an optimization scheme that creates directions that are as isotropic and distinct as possible leading to a sparse but uniform representation. With this approach it is also possible to complement any given set of isotropic as well as random directions, allowing to converge the representation of the nuclear configuration space efficiently. The approach is demonstrated by the development of a full-dimensional PES of formaldehyd and corresponding vibrational dynamic calculations.

Chiral Crystal Packing Induces Enhancement of Vibrational Circular Dichroism

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Vibrational circular dichroism (VCD) has enriched the toolbox of analyzing and classifying chiral supramolecular organization due to its outstanding sensitivity towards absolute and relative configurations and its ability to resolve induced chirality in originally achiral regions. In *ab initio* molecular dynamics (AIMD) simulations, the potential-energy surface of the phase space is sampled impartially as a statistical ensemble including entropic effects. Important progress has been made in the field of AIMD-based vibrational spectroscopy, in which IR and VCD spectra are obtained as Fourier transformed time-correlation function.

Our AIMD simulations of anharmonic solid-state VCD spectra of L-alanine crystals reveal how coherent vibrational modes exploit the space group's chirality, leading to non-local, enhanced VCD features–most significantly in the carbonyl region of the spectrum. The VCD-enhanced signal is ascribed to a helical arrangement of the oscillators in the crystal layers. No structural irregularities need to be considered to explain the amplification, but a crucial point lies in the polarization of charge, which requires an accurate description of the electronic structure.

Delivering a quantitative atomic conception of supramolecular chirality induction, our *ab initio* scheme is applicable well beyond molecular crystals, for example, to address VCD in amyloid fibrils and related compounds.



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Intersystem-Crossing and Luminescence properties of Triarylboranes

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Triarylboranes can be used as strong electron acceptors in conjugated organic fluorescent materials, due to their empty boron p orbital [1]. Lately, phosphorescent triarylboranes were synthesized exhibiting high triplet quantum yields and radiation lifetimes of a few seconds [2].

In this work, we investigate photorelaxation pathways to gain insights into the efficient triplet generation process. Due to fluorescence rate constants of the order of about 10^8 s^{-1} , intersystem crossing (ISC) needs to be faster to explain the phosphorescence. The brightest singlet state is the S₁ state and lying beneath we found six triplet states employing the combined density functional and multi-reference configuration interaction (DFT/MRCI) [3, 4] method. The potential energy surface of three of these triplet states (T₄, T₅, T₆) cross the S₁ state along the linear interpolated path from S₀ to S₁ and can lead to fast ISC. In contrast, the electronic excitation in tri-phenylborane deactivates via a concial intersection between S₁ and S₀. Phosphorescence radiation lifetimes were computed at the density functional theory and multi-reference spin orbit configuration interaction (DFT/MRSOCI) [5] level and agree well with experiment.



Figure 1: Triarylborane Derivates

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Optical properties of open-shell molecules with CASSCF response theory

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An implementation of electronic excitation energies and transition moments to simulate UV/Vis and electronic circular dichroism (CD) spectra is presented for the CASSCF linear response method.[1, 2] We focus on applications to transition metal complexes where open-shell electronic structures are frequently encountered and require multi-reference complete active space (CAS) wave functions to achieve at least qualitative accuracy. Hermicity of all intermediates in the calculation is preserved and partially exploited,[3] which makes the calculation of the multi configurational random phase approximation (RPA) nearly as efficient as when invoking the Tamm–Dancoff approximation. To accelerate calculations of molecules with 100 atoms and more, the resolution-of-the-identity (RI) approximation is used for the integral transformation. Furthermore, the Coulomb part of the Fock matrices is computed with the RI approximation while the exchange part is built in a semi-numerical fashion with the chain-of-spheres approximation.

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Structural Evolution of Sulfur-Copolymer Cathodes in Lithium-Sulfur Batteries Studied by Theoretical and Experimental NMR Spectroscopy

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Sulfur with its high theoretical lithium capacity of 1675 mAhg⁻¹ is an abundant and low-cost element. For these reasons, lithium-sulfur (Li-S) batteries are among the most promising next-generation energy storage devices.[1] However, low sulfur utilization and poor cycle life are among issues limiting commercialization of the Li-S batteries. These problems are mainly related to dissolution of Li-polysulfides (Li₂S_x, $2 \le x \le 8$), which form during discharge cycles, into the electrolyte before full reduction to Li₂S. Migration of the Li-polysulfides to the anode (*shuttle effect*), their reaction with lithium and eventually formation of an insulating layer of Li₂S₂ and Li₂S around the anode can also obstruct the diffusion of Li⁺ cations into the electrolyte. Additionally, volume variation of the S cathode upon reaction with Li ions, which is related to different densities of elemental α -sulfur (2.07 g cm⁻³) and Li₂S (1.66 g cm⁻³) not only results in loosened electrical contacts with the conductive substrate, but can also lead to safety problems. In recent years, researchers have proposed various approaches to overcome these shortcomings.

Sulfur-copolymers are promising alternative cathode materials to elemental sulfur as they provide high reversible capacity. Moreover, their structural flexibility can withstand the volume expansion during the discharge. However, the redox mechanisms of these materials are not well understood owing to the difficulty in characterizing amorphous structures and identifying individual ionic species. Here, we use quantum mechanical calculations to simulate NMR chemical shifts to investigate the structural evolution of the prototypical S-copolymer cathodes, sulfur-diisopropenylbenzene copolymers (poly(S-co-DIB)), during cycling.[2] We demonstrate that the polysulfides with different chain lengths can be distinguished by ¹³C NMR spectroscopy, revealing that the structure of the copolymers can be tuned in terms of polysulfide chain lengths and resulting reaction pathways during electrochemical cycling. The dependence of the chemical shifts on the S-chain length is also confirmed by our solid-state NMR spectroscopy experiments. Our results show that the improved cyclability of these cathodes originates from the role of organic moieties acting as anchors that fixate polysulfides to the polymeric network during cycling, thus hindering the shuttle effect. This work provides a new methodological concept for the mechanistic studies to track the intermediate species in Li-S batteries.

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Improving the Stability of EDA with Local Orbital Spaces

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Understanding intermolecular interactions has always been a central topic to theoretical chemistry, from the smallest systems to supramolecular chemistry. This knowledge is vital in guiding the design and synthesis of new molecular constructs or in the interpretation of complex spectra, may it be in the gas phase, solution or condensed phase. Over the years, several schemes have been presented to dissect the different forces at play, including the seminal work by Kitaura and Morokuma or later the powerful family of SAPT approaches. For some time now, in parallel to these developments, use has been made of local orbital based analysis to separate the different energy contributions. No matter what scheme is picked, a few properties should be kept. 1) the separation of energy terms should sum to the total interaction energy, 2) the analysis should converge with an increasing level of theory (may it be the method or the basis set), 3) generally applicable to any molecular aggregate.

Local orbital analysis tends to suffer from some arbitrariness due to the choice of how some of the orbital space is separated. This is easily linked to the choice of localization method and the way the different orbitals are tagged to coordinate space.

We investigated an energy decomposition scheme for PNO-LMP2, similar to the LED approach by Neese et al. [1]. Our main focus lies in the fulfillment of the upper defined properties. Herein, we are able to demonstrate the stability of our approach and also present visual analyzation tools to ease the interpretation.

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The intramolecular hydrogen bond in p-substituted o-(Ndiethyl)aminomethylphenols:Combined a DFT, QTAIM and ELF investigation

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The aminomethylphenols are commonly used in the synthesis of medicaments with multiple pharmacological activities and as catalysts for supramolecular systems, epoxy resins. The availability of the intramolecular contacts causes the specificity of physicochemical properties of the aminomethylphenols. The intramolecular O-H...N bond in the various p-substituted o-(Ndiethyl)aminomethylphenols, o-DEAMPH, o-N (C₂ H₅)₂CH₂C₆ H ₅X (X=p-OCH ₃, CH₃, H, F, Cl, Br, COCH₃, COOCH ₃, CN and NO₂) were investigated by means of theoretical calculations in the gas phase. The molecular geometries in the equilibrium state and vibrational frequencies were calculated by density functional theory (DFT) at the B3LYP 6-311+G (d,p) level of theory. The calculated infrared spectra of o-DEAMPH revealed of the O-H stretching vibrational frequencies red shift. It is found that the linear correlation between the O-H stretching vibrational shifts, $\Delta v (\Delta v = v_{\text{PHENOL}} - v_{\text{PHENOL}})$ v_{DEAMPH}) and the experimental ¹H NMR chemical shifts of the hydroxyl protons, $\Delta\delta(\Delta\delta = \delta v_{\text{DEAMPH}} - \delta \delta v_{\text{DEAMPH}})$ v_{PHENOL}): $\Delta v = -174.049 + 108.450 \Delta \delta$ (R^{2=0.9956}). The intramolecular hydrogen bond energy estimated using Jorgansen ratios was from 6.6 to 8.0 kcal / mol. The quantum theory atoms in molecules (QTAIM) and the theory of the electron localization function (ELF) were employed to characterize and quantify intramolecular interactions. By using these analyses it is found that the critical points positions characteristic of intermolecular contacts obtained by QTAIM and ELF are very similar each other. The estimation of the hydrogen bond energy by the Espinosa method results in occur a values 9.9-12.6 kcal/mol. This method are systematically overestimated for the H-bond energy, as demonstrated slope relationship between the hydrogen bond energy obtained from the experimental ¹H NMR, E_{exp} and predicted topological, E_{QTAIM} energy is 1.34($R^2 = 0.9959$). The linear correlation between energy of the hydrogen bond and Hammett substituent constants, σ_p was observed (R² =0.9926). Considerable interest has attached to excellent correlation between predicted the IR spectroscopic data, Ev and the parameters calculated within the QTAIM, total energy density $\rho^{\rm BCP}$ and the density of potential energy V: Ev=-4234.37-24929.2 ρ^{BCP} (R²=0.9988), $Ev=3948.7+21915.7V(R^2=0.9988)$, which can be used for estimation of O-H...N bond energy.Moreover, numerous relationships between the hydrogen bond energy and the universal descriptors of hydrogen bonds: d_{H...N} (R²=0.9982), \angle _{O-H...N} (R²=0.9919) as well as the core-valence bifurcation index CVB (based in ELF, $R^2 = 0.9964$) were obtained. In addition to intramolecular Hbond, in the diethylamine fragment of o-DEAMPH molecules there is hydrogen-hydrogen (H....H) interaction between the ethyl substituents. Such interactions are caused by the peculiarities of the spatial arrangement of ethyl substituents. It is obvious that these bonds are fragile (1.32 - 1.32 kcal/mol).

Regioselective B₁₂-Catalyzed Aromatic Dehalogenation Predicted by Density Functional Theory

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Anaerobic bacteria may gain energy through the reductive dehalogenation of otherwise persistent aromatic halides.^[1] In this so-called dehalorespiration, the supernucleophile cob(I)alamin of vitamin B₁₂ serves as biochemical catalyst, exploiting apparently speciesspecific electron transfer (ET) processes from B_{12} Co^I to the substrate for its regioselective stepwise dehalogenation. The associated mechanisms discussed so far include primary attack at either halogen or hydrogen with respective implications for the rate-determining step and its dependence on electronic structure characteristics.^[2, 3] The present study focuses on 10 aromatic chlorides and bromides dehalogenated through Dehalococcoides strain CBDB1 that still lacks crystal structures of cob(I)alamin-substrate complexes as basis for clarifying the mechanistic details. To unravel the most likely reaction mechanism, density functional theory (DFT) at the UB3LYP*/Def2TZVPP//UBP86/Def2SVP level of theory has been applied to respective reactions of a truncated B_{12} Co¹ model with the substrates. To this end, Grimme D3 dispersion, zero-point energy (ZPE), thermal and basis set superposition error (BSSE) corrections were included, without and with simulating the protein environment through the COSMO variant CPCM ($\varepsilon = 4$) implemented in Gaussian 09. The approach extends earlier studies of mechanisms underlying cytochrome P450 catalysis.^[4, 5] The calculations show that outer-sphere ET mechanisms according to the Marcus theory can be ruled out energetically. Regarding inner-sphere ET routes, our results strongly suggest a proton-coupled two-electron transfer (PC-TET) mechanism yielding B₁₂ Co^{III} and the dehalogenated metabolite, followed by two 1-electron reductions to regenerate B_{12} Co^I for a next catalytic cycle. In particular, the computational model can fully explain the experimentally observed regioselectivity. The discussion includes computational chemistry analyses of the underlying kinetics and thermodynamics, and theoretically derived implications for non-halogen substituent effects.

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Rotational tunneling of coupled methyl quantum rotors: single rotor potential versus coupling interaction

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At low temperature, methyl groups act as quantum rotors with quantized rotational states. Especially the large energy difference between the ground and first excited rotational states in 4-methlpyridine has been subject of experimental studies in inelastic neutron scattering (INS) [1] and in the context of hyperpolarization techniques in NMR spectroscopy [2, 3].

Here, we present a theoretical explanation for the multiple structure of the rotational tunneling peaks[1] observed in INS experiment of 4-methylpyridine within a coupled-pair model [4]. The focus is on the effect of chemical environment (molecular packing) on the rotational states. In particular, we study the influence of coupled motion of methyl rotators on the tunnelling spectrum. In this regard, the potential energy surface (PES) of methyl rotations is obtained through a set of combined first principles and nudged elastic band calculations [5]. The quantum rotational energy levels are obtained by the numerical solution of two-dimensional time independent Schrödinger equation for the calculated PES. Our computed energy levels reproduce the observed tunneling transitions in 4-methylpyridine in well agreement with experiments. Furthermore, we have simulated the interaction of two adjacent methyl groups within an analytical form for the coupled methyl groups composed of single rotor potential and coupling interaction terms. It is found that the main determinant factor controlling the splitting energy levels is the ratio of strengths of coupling and single rotor potential terms. By mapping the calculated PES profile of 4-methylpyridine on the analytical model, it turns out that the large tunnel splitting observed in 4-methylpyridine results from its weakly hindering potential with proportionally shallow single potential to coupling interaction.

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Oligomers on nanostructured surfaces: Adsorption-induced alteration of the surface reconstruction

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Theoretical studies of organic adsorbates on metal surfaces have mainly focused on the adsorption of small molecules on ideal surfaces. However, many surfaces, e.g. low index surfaces of Au, Ir, and Pt, have complex reconstructions that are challenging for surface science studies. In this work, we approach such complex (or nano-structured) surfaces with a combination of density-functional theory (DFT) calculations and scanning tunnelling microscopy (STM) measurements for the example of the α -sexithiophene (α -6T) oligomer adsorbed on the reconstructed Au(100) surface. We find that due to its corrugation pattern the reconstructed Au(100) surface offers a wide range of adsorption sites than can be broadly classified into on-ridge and in-valley types with energetic adsorption preferences for the latter. Surprisingly, adsorption in energetically ill-favored on-ridge positions leads to strong alterations of the surface reconstruction, facilitated by the "soft" nature of gold. As a result of electrostatic effects and charge transfer between the surface and the molecule, α -sexithiophene pushes the ridge out of the way rather than to slide down its side into the valley.

Differential spin state stabilization of carbenes by hydrogen and halogen bonding: a DLPNO coupled cluster study

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Carbenes are divalent carbon species where two electrons are distributed into two nearly degenerate orbitals. This results in close lying singlet and triplet spin states, which display different properties and reactivity. The singlet state has a significant difference in distribution of electron density into two orbitals. This leads to zwitterionic character where two differently charged sites have the ability to react as both a Lewis acid and base, whereas the triplet carbene is believed to behave as a radical. Crucially, the explicit interaction of the singlet state with hydrogen and halogen donors leads to stabilization that can often switch the ground state of triplet carbenes to singlet. In this study we use the domain-based local pair natural orbital (DLPNO) approximation of coupled cluster theory and its local energy decomposition (LED) feature to compute accurate energetics at the coupled cluster level and further analyze these energetics to get insights into the formation of halogen and hydrogen bonds in carbenes and their effects on the singlet-triplet splitting.

8.2. Poster Session B

Trajectory simulation of the reverse processes of a recombination of the ions which are formed at collision dissociation of two neutral molecules

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Collision-induced dissociation in system CsCl + RbJ which is followed by disintegration of one or both initial molecules and formation of new both ionic, and neutral products can proceed according to the following 11 channels (direct reactions from left to right on arrows):

1.	$CsCl + RbJ \iff$	$Cs^+ + Cl^- + Rb^+ + J^-$
2.	\leftrightarrow	$Cs^+ + Cl^- + RbJ$
3.	\leftrightarrow	$Rb^+ + J^- + CsCl$
4.	\leftrightarrow	$CsJ + Rb^+ + Cl^-$
5.	\leftrightarrow	$RbCl + Cs^+ + J^-$
6.	\leftrightarrow	CsJ + RbCl
7.	\leftrightarrow	$CsClRb^+ + J^-$
8.	\leftrightarrow	$CsClJ^{-} + Rb^{+}$
9.	\leftrightarrow	$CsJRb^+ + Cl^-$
10.	\leftrightarrow	$RbJCl^{-} + Cs^{+}$
11.	\leftrightarrow	CsClRbJ

Dynamics of all these channels is considered in detail in [1] on the basis of trajectory models. Figure 1 represents the dependence of summary probability of the reverse processes (from right to left) of a recombination of ions with formation of molecules CsCl and RbJ on collision energy of particles.



Fig.1. Dependence of summary probability of the reverse processes of ion recombination on collision energy of particles.

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Ρ4

On the physisorption of water on graphene: Sub-chemical accuracy from many-body electronic structure methods

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Molecular adsorption on surfaces plays an important part in catalysis, corrosion, desalination, and various other processes that are relevant to industry and in nature. The adsorption energy of water on graphene is particularly interesting as it calls for an accurate treatment of electron correlation effects. Combined with the vanishing band gap, this poses practical challenges to experiments and simulation methods. We have recently shown that improved algorithms for diffusion Monte-Carlo (DMC) made the prediction of chemically accurate lattice energies for molecular crystals feasible [1].

Here, we employ diffusion Monte-Carlo (DMC) as well as the random phase approximation (RPA+GWSE) for calculating adsorption energies of water on graphene [2]. Additionally, water adsorption on benzene and coronene is investigated using DMC, RPA, and linear scaling coupled cluster (CCSD(T)). Different adsorption motifs on graphene have a very similar binding energy though the contributions to the interaction are quite distinct as shown by charge density analysis and symmetry adapted perturbation theory. The binding energies from the many-body electronic structure methods agree within sub-chemical accuracy, our best estimate from DMC is -99 ± 2 meV. The vanishing band gap makes the convergence of the substrate towards the periodic graphene layer particularly slow and thus binding energy estimations from small clusters unreliable (see Fig. 1). Most van der Waals inclusive DFT methods yield reasonably accurate results for the finite clusters. In contrast, beyond atom-pairwise van der Waals interactions seem to be necessary to capture all details of the different binding motifs on graphene [3, 4].



- Fig. 1: Convergence of water adsorption energies on increasingly large substrates. DMC binding energies are shown as a function of the inverse substrate radius. The extrapolating lines using benzene and coronene data highlight the slow convergence.
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Metal functionalized [2,2]paracyclophane and BN-substituted [2,2]paracyclophane for hydrogen storage in energy application

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Hydrogen is the most promising candidate for a sustainable energy source in the transport sector. Storage of hydrogen is the main obstacle for it to be used as a fuel. A DFT approach to test the hydrogen storage capacity of [2,2]paracyclophane (PCP22) and BN-substituted PCP22 is presented here. Electronic structure calculations were performed on Li and Sc functionalized on the delocalized pi-electrons of benzene rings in PCP22, as well as Sc and Ti functionalized on delocalized pi-electrons of borazine in BN-substituted PCP22. These metal functionalized systems were studied for hydrogen storage efficiency by using the M06 hybrid functional and 6-311G(d,p) basis set. Transition metals Ti and Sc coordinate with borazine and benzene through Dewar interaction. The binding energy for Sc metals functionalized on PCP22 was 2.70 eV while for Li, it was 1.19 eV. The binding energy for Ti functionalized on BN-substituted PCP22 was 1.73 eV while for Sc it was 0.23 eV. Weaker binding energy values in borazine are due to its lesser aromaticity than the benzene. Hydrogen saturated Sc functionalized PCP22 adsorbed a maximum of 10 hydrogen molecules with hydrogen wt.% of 11.8 and in Li functionalized PCP22 maximum 8 hydrogen molecules were adsorbed 13.7 wt.% with 0.05 eV desorption energy in both the cases. In BN-substituted PCP22 the maximum hydrogen wt.% was calculated to be 9.88 % with desorption energy 1.01 eV when functionalized with Ti and held a maximum of 10 hydrogen molecules and 0.31 eV desorption energy with 8.91 % when functionalized with Sc adsorbing 8 hydrogen molecules and attaining saturation. All the complexes carry higher hydrogen storage capacity than 7.5% which is a target specified by Department of Energy, US for the year 2020. Stability of these complexes was tested with vibrational frequencies which were found positive values for all the complexes. Conceptual DFT study predicted that global reactivity parameters obey "maximum hardness and minimum electrophilicity principle" which confirmed the high stability of all saturated complexes. ADMP simulation study proved that within the temperature range of 300-400 K all the hydrogen molecules desorb from these complexes. This signifies their sorption reversibility and ease of on-board generation. These results imply the potential of paracyclophanes and BN-substituted paracyclophanes as an excellent hydrogen storage material.

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QM/MM Investigation of the Functional Role of a Second Coordination Shell Arginine Residue in [NiFe]-Hydrogenases

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The oxidation of H_2 ($H_2 \rightleftharpoons 2H^+ + 2e^-$) catalyzed by [NiFe]-hydrogenases has been extensively studied both experimentally and computationally. However, the functional role of an arginine residue strictly conserved near the active site of these enzymes is not yet well understood. In a recent study on hydrogenase-1 from *E. coli* (EH1) [1], mutation of this residue (R509) by lysine was shown to reduce the enzyme activity by >100-fold. Considering this result and the strong basicity of the guanidine group, R509 has been proposed to be in a deprotonated form and to act as a base during the heterolytic H_2 activation step (Figure 1) [1]. This is in contrast with the generally accepted textbook knowledge of arginine being protonated, and it can either play a stabilizing role or take part in a putative proton transfer pathway during catalysis.

In this work, we present molecular insights into the functional role of R509 on H₂ activation by EH1. A quantum mechanics/molecular mechanics (QM/MM) approach was used to compute the deprotonation energy of R509. QM/MM calculations were also performed to compute the reaction profiles of the H₂ activation with either R509 or the terminal nickelcoordinating cysteine residues (C76 and C576; Figure 1) acting as the proton acceptor. In QM/MM geometry optimizations and reaction profile calculations the MM region was treated using the CHARMM forcefield and density functional theory (BP86/def2-TZVP) was used to treat the QM region. For further validation, we carried out single point calculations at the BP86-D3, B3LYP-D3, and TPSSH-D3 levels of theory for all relevant geometries [2].



Figure 1. Proposed role of R509 in the H₂ activation step in EH1 [1].

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Local coupled cluster theory applied to noncovalent interactions in real life chemistry. From numbers to chemical insights.

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Local correlation techniques exploit the short range nature of dynamic electron correlation to reduce the inherent steep scaling of correlated wavefunction based methods. In particular, the DLPNO-CCSD(T) method allows one to perform single point energy calculations for systems with hundreds of atoms while typically retaining about 99.9% of the canonical CCSD(T) correlation energy. Unfortunately, the CCSD wave function is a highly complex object whose physical interpretation is not immediately apparent. Hence, in order to facilitate the interpretation of local coupled cluster results, we have recently introduced the local energy decomposition (LED) analysis. [1] This scheme allows one to decompose the DLPNO-CCSD(T) interaction energy between two (or more) interacting fragments into chemically meaningful contributions, thus providing a useful interpretative framework in which to discuss experimental observables related to the nature of the interaction. In this work, some recent developments and applications of the LED methodology in the context of noncovalent interactions are shown. In particular, this scheme is used to elucidate the role of London dispersion in affecting the structural stability of Frustrated Lewis Pairs (FLP) [2] and agostic complexes. [3] Moreover, the interplay of covalent and noncovalent bonding contributions in affecting the relative stability of a series of H-bonded dimers is discussed. The series includes model systems of importance for gaining understanding of the basic principles of the interaction [4] as well as large adducts of several interacting molecules with practical interest in organocatalysis and biology. [5-6] In all cases, the results obtained are used to rationalize a series of previously published experimental findings.

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X-ray emission spectroscopy in the algebraic-diagrammatic construction framework

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The algebraic-diagrammatic construction (ADC) approach provides a series of hierarchical *ab initio* methods based on perturbation theory, formulated for the calculation of excited states and excited state properties. It has been successfully applied to a plethora of spectroscopies [1], including X-ray absorption spectroscopy [2] and resonant inelastic X-ray scattering [3], and we here present the first application of ADC to non-resonant X-ray emission spectroscopy (XES). Using a scheme previously adopted for time-dependent density functional theory and equation-of-motion coupled cluster [4], the wave function of a core-ionized system is formed using the maximum overlap approach [5]. With this as a reference, the valence-to-core transitions occur at negative eigenvalues using standard unrestricted ADC. The approach has been applied to X-ray emission spectra of a set of small molecules (featuring transitions to the 1s core-hole of six different elements), and a mean error of 0.07 eV is achieved using ADC(2). A standard deviation of 0.46 eV is reported, and both the mean error and the standard deviation increase when adopting the higher-order ADC(2)-x and ADC(3) schemes. This behaviour is attributed to a fortuitous error cancellation at the ADC(2) level of theory.



Fig. Oxygen *K*-edge X-ray emission spectra of gas phase water, as calculated for 25 structures obtained by *ab initio* molecular dynamics and compared to experimental measurements [6].

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Restricting Solvation to Two Dimensions: Soft-landing Microsolvated Ions on Inert Surfaces

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Understanding the impact of surfaces on the H-bond topology of microsolvated ion clusters remains a challenge. In order to decipher such dimensional restriction effects, we introduce and study a well-controlled model system that decouples the intricate chemical interaction phenomena from those physical effects that emerge solely from restricting the spatial dimensions from three to two. With the aim to stimulate future experimental investigations, this is accomplished by simulating the deposition microsolvated Na⁺ and Cl⁻ ions, on a xenon surface grown on a copper support using ab initio molecular dynamics. By comparing deposited microsolvated ions to their gas phase references, we have found remarkable changes for Na⁺ solvatomers, while the microsolvated Cl⁻ clusters remained intact on the surface. Energy correlation analyses have shown that the microsolvation shell of the cationic clusters imprints arrangements of water molecules that are unfavorable for H-bonding, thus readily leading to deformations of the H-bonding network after deposition, even providing structures that are unfavorable in the gas phase. In stark contrast, the anionic clusters are characterized by strongly attractive water-water interactions, which allow only for insignificant changes upon soft-landing. Given its fundamental nature, the discovered phenomenon is expected to be general rather than specific to the particular system classes investigated.

Using the GW/BSE scheme to describe van der Waals interactions

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The GW/BSE method based on the Hedin equations (GW) and the Bethe-Salpeter equation (BSE) has began to develop into a useful tool for quantum chemists in the last decade. In a perturbational approach, starting from a Kohn-Sham (KS) reference state, GW can be used to obtain quasiparticle (QP) energies that describe ionization potentials and electron affinities of each KS orbital. Based on these perturbational QP states the BSE can be used to obtain the response function of a given system. In contrast to many functionals used in time-dependent DFT the GW/BSE ansatz is able to describe charge-transfer (CT) and Rydberg excitations, which has been demonstrated in Ref. [1]. While this behaviour is mandatory to describe CT excitations in non-covalently bonded complexes, see Fig. 1, also interaction energies of van der Waals complexes can be obtained using the GW/BSE method. It has been shown that within the symmetry-adapted perturbation theory (SAPT) the required monomer response can be expressed in terms of GW/BSE polarization functions, and that "GW-SAPT" improves over its DFT-SAPT pendant while retaining the same overall scaling [2].



Figure 1: Hole (left, red/blue) and particle (right, green/orange) NTOs of the 2 ¹A₁ excited state in the non-covalently bonded complex C₆H₆-TCNE (BSE@qsGW/def2-TZVP).[1]

Further, if the efforts made on quasirelativistic SAPT [3] and GW-SAPT are combined, calculations of dispersion energies in strong magnetic fields are possible. The generality of the ansatz allows for an accurate descriptions of many effects (spin-orbit, charge-transfer, magnetic fields) at once.

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Quantum effects on the structures and dynamics of small cyclic molecular rotors imposed by the molecular symmetry group

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The familiar list of quantum effects in molecular dynamics includes zero point energies, tunneling, and interferences of wavepackets. We show that for systems with cyclic internal motions of identical nuclei, such as small cyclic molecular rotors consisting of $N \ge 2$ identical atoms like methyl groups or planar boron rotors, e.g. ${}^{11}B_{11}^-$ or ${}^{11}B_{13}^+$, this list needs to be extended. For these systems, the potential energy surfaces support N_t equivalent global minimum (GM) structures, separated by N_t equivalent transition states [1]. Classical molecular dynamics (MD) simulations of such systems inevitably start out from a single GM [2, 3, 4, 5]. We show, however, that a state being localized in a single GM is unphysical, because these type of clusters exist in form of nuclear spin isomers. This is a consequence of the molecular symmetry of the systems, and of the fact that, to very good approximation, it is impossible to generate superposition states of different nuclear spin isomers [6]. It follows that all previous MD simulations of such systems, including simulations of laser driven unidirectional rotational/pseudo-rotational motions [2, 3], do not only suggest a wrong physical picture, but they also falsely predict observables. For example, nuclear spins prohibit laser ignition of the rotations of the molecular rotor. The quantum dynamics of nuclear spin isomers is fundamentally different from traditional classical MD simulations. We exemplify this quantum effect for the boron rotors ${}^{11}B_{11}^-$ and ${}^{11}B_{13}^+$.

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Hierarchical Bonding Pattern in the Thermoelectric Material Ag₆Ge₁₀P₁₂

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Ag₆Ge₁₀P₁₂ is the prototype of a class of ternary phosphides with a pronounced bonding hierarchy and, as a consequence, remarkable thermoelectric properties. The compound contains two types of germanium atoms. One type (Ge⁴⁺) is linked to phosphorus, forming a covalent, zinc blende like framework including large voids. The other type (Ge²⁺) is capping subvalent [Ag₆]⁴⁺ octahedra, being located in the voids. The hierarchy of bonding types with a wide range of bond strength together with a peculiar phonon spectrum give rise to a very low lattice contribution to the thermal conductivity, $\kappa_L < 1$ W/m·K, and thus to a thermoelectric performance with a remarkably high figure of merit (*zT*) of about 0.6 at 700 K [1].



With the interpretation of bonding descriptors derived from density functional bandstructure calculations, combined with the analysis of the computed phonon density of states and their projections onto the various atom types, a consistent bonding picture can be elaborated.

Substitution of various atoms in the parent compound, $Ag_6Ge_{10}P_{12}$, allows for a controlled modification of the bonding properties. Substituting Ge^{4+} by Si^{4+} leads to an overall stiffening of the covalent framework. Taking Sn as the capping tetrel, a blue-shift of the low-lying phonons is computed, together with a decrease of the band gap (0.8 eV \rightarrow 0.3 eV).

Contrasting the computed variations due to the atomic substitutions with the related thermoelectric data will help to understand the complex interplay of electronic and dynamical properties in thermoelectric materials

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Steps in Heterogeneous Catalysis and Their Anomalous Role in the Dissociation of D₂ on Copper Surfaces

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Steps on metal surfaces are usually expected to exhibit an increased catalytic activity for bond cleavage of small molecules over their flat single-crystal counterparts [1, 2, 3]. In this contribution, we demonstrate that the prototypical reaction of molecular hydrogen on Cu surfaces contradicts this notion. Using state-of-the-art dynamics calculations and molecular beam experiments, we surprisingly observe the dissociation of D_2 to occur less likely on the stepped Cu(211) surface than on the flat Cu(111) surface [4]. Based on theoretical analyses, we suggest that this exceptional behavior is due to a geometric effect. Very recently, independent experiments performed on the system confirm the novel observations [5, 6]. We hope that this will help to establish a new view on surface imperfections and their capacity to promote heterogeneously catalysed reactions.

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Mixed Aluminium Iron Oxide-Clusters: Structures and Vibrations

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After the investigation of several pure aluminum and iron oxide clusters and their adsorption of few water molecules we now present our first results on mixed clusters of the composition $(Al_2O_3)_nFeO^+$ with n = 1-5. In this combined study we use infrared photodissociation (IRPD) spectroscopy at cryogenic temperature together with a genetic algorithm relying on density functional theory (DFT) for structure generation to measure and identify small metal oxide clusters by means of their vibrational features. Particular attention has to be turned to the proper description of the electronic structure of the iron center and the possibility to have several low and high spin electron configurations. To this end coupled-cluster calculations are used to refine the DFT results.

By the comparison of TPSSh and B3LYP calculations it is shown that the predicted vibrational spectra do not change much depending on the density functional while the energetical order of different isomers is very sensitive to the used method. Structural motifs found for the pure Al-O and Fe-O clusters of the corresponding composition are also predicted for the mixed oxides to form stable minima. But from the agreement with the measurement it can be concluded that not always the most stable structure on DFT level is the true global minimum of a certain composition. Furthermore, the exchange of a single Al atom by an Fe atom has significant effects on the structural properties of the smaller clusters (n = 1, 2) but not on the bigger ones. For the clusters with $n \ge 3$ it is possible to compare different positions of the iron atom in the same isomer frame. Occasionally, there are very unfavorable sites for iron, especially those where it is more than three-fold coordinate by oxygen and where there is a certain strain on it by the molecular framework. Bigger dihedral angle than those found for the Al atoms are preferred. However, nearly planar oxygen coordination of iron is again energetically unfavorable.



Figure 1: Assigned structures of $(Al_2O_3)_nAlO^+$ and $(Al_2O_3)_nFeO^+$ clusters.

Relativistic Effects in the Heaviest Element of the Periodic Table (and why it should not be called a Noble Gas)

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Spin-orbit relativistic effects cause the outer electron shells in oganesson, which is the heaviest element of the Periodic Table of Elements, to smear out and approach the Fermi-gas limit.[1] A way to visualize this is by computing the Electron Localization Function (ELF). This behavior has a major impact on the physical and chemical properties of this elusive element. [2]



Figure 1: ELF in the Xe, Rn and Og atoms as calculated by Four-component DHF theory.

We computed many-body interaction potentials for oganesson with state-of-the-art relativistic coupled cluster method up to full quadruple excitations utilizing non-relativistic, scalarrelativistic and spin-orbit relativistic theories, respectively. The two-body potentials of the Extended Lennard-Jones type differ significantly when compared with each other with respect to equilibrium distances and dissociation energies, demonstrating the remarkable impact spinorbit effects have on the structure of the valence electron shells and the polarizability of Og.[1] The ramifications of it are illustrated by calculations of thermodynamic properties of solid-state oganesson via sophisticated Monte Carlo simulations which reveal the drastically different behavior compared to the lighter homologues. Our studies highlight the prime importance of including spin-orbit effects when calculating heavy and super-heavy elements.

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Molecular Docking, Molecular Modeling, Vibrational and Biological Studies of Some New heterocyclic α-Aminophosphonates

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Diphenyl (aryl) (N-quinazolin-4-yl-hydrazino) methyl phosphonates 3a-3d were synthesized. The newly synthesized compounds exhibit a remarkable inhibition of the growth of Grampositive, Gram-negative bacteria and fungi at low concentrations. The cytotoxicity of the synthesized compounds showed a significant cytotoxicity against the breast cancer cell line (MCF7). Also, the quantum chemical calculations showed that the presence electronwithdrawing substituent increases the biological activity of the α -aminophosphonates amongst all investigated compounds which are in a good agreement with the experimental results. Also, a good agreement between the experimental FT-IR and the calculated ones was found. From NBO study, the movement of π -electron cloud from donor to acceptor, i.e., intramolecular charge transfer can make the molecule more polarized and the ICT must be responsible for the NLO properties of the molecule. Therefore, the titled compounds may be used for nonlinear optical materials application in future as discussed in the quantum chemical parameters section. Finally, according to Fukui indices, the most nucleophilic site in the most biologically active compound **3b** is N7, N9, O20, O27 and O34 atoms (positive value i.e. $\Delta f(r) > 0$). Similarly, the electrophilic attack site is C12, P19 atoms (negative value i.e. $\Delta f(r) < 0$). On the other hand, N7, and N9 atoms are the softest atoms in the molecules that have the highest local softness ΔS value which indicates these are the most active sites in the molecule. Molecular docking study showed that compound **3b** has different types of interactions with the enzyme.



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Abstract

We examined the cyanide anion (CN⁻) sensing mechanism of 3,5-diformylborondipyrromethene (1) by calculating the photophysical properties of 1 and 2 (cyano addition product of 1) with density functional theory (DFT) and time dependent-density functional theory (TD-DFT) methods using Gaussian 09 programs package. The negative values of energy changes (ΔE) and the free energy changes (ΔG) confirmed the feasibility of CN^- addition. The blue-shifted UV-vis spectra calculated for 1 and 2 show a good agreement with earlier reported results [1]. 1 and 2 show different excited state deactivation process as predicted by TD-DFT computations which designate the first excited state of **1** as a coplanar local excited state with π - σ^* transition. A slight charge separation character in the first excited state of 2 and loss of coplanarity at the formyl groups pave the pathway for non-radiative deactivation of the excited state and under their synergistic effect, the fluorescence of 1 after the CN⁻ addition is quenched notably. Thus, the different excited state features of 1 and 2 play a role in the CN^{-} sensing mechanism of 1. Furthermore, it is experienced that out of the functionals employed here in this contribution (i.e., PBEPBE, CAM-B3LYP, M06-2X and LSDA) [2-5] DFT and TD-DFT computations performed at PBEPBE/6-311+G(2d,p)//PBEPBE/6-311G(2d,p) and CAM-B3LYP/6-311+G(2d,p)//CAM-B3LYP/6-311G(2d,p) levels respectively are adequate for reproducing the excitation and fluorescence energies with a fine accuracy. Using this methodology, we designed an aza-BODIPY (3) which shows a fluorescence enhancement on cyanide binding (4) involving intramolecular charge transfer and partial configurational changes and it is for the synthetic chemists now to synthesize the designed molecule 3 for cyanide sensing in particular. This employed method can again be utilized for calculating the absorption and emission spectra of BODIPYs and its derivatives and it may pave a way for the designing of new potential BODIPY based anion sensing molecular candidates.



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Relativistic TD-DFT calculations for non-linear optical properties

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Non-linear optical properties of molecules are of great interest in modern materials science and medicine. While two-photon absorption (TPA) is relevant e.g. for photochromism or photodynamic therapy of cancer, second harmonic generation (SHG), which corresponds to the first hyperpolarizability, plays an important role for frequency manipulation of lasers. For example, every green laserpointer contains a crystal which by SHG upconverts the infrared emission of a semiconductor laser to green.

For this reason materials with strong TPA and SHG are the goal of a lot of molecular design studies which are often supported by quantum chemical calculations. The number of programs which are capable of such calculations is not large, however when it comes to the treatment of relativistic effects, no efficient and reliable computational approach is available.

As many compounds with promising non-linear optical properties contain heavy elements, a proper treatment of relativistic effects is indispensible. The strong effect of relativistic effects on spectroscopical properties in general is illustrated by a daily-life example: Quantum chemical studies have shown that the characteristic color of metallic gold is completely caused by relativistic effects. In calculations which neglected relativistic effects, gold turned out to have the same color as silver.

In this presentation, a TD-DFT approach for the calculation of TPA and first hyperpolarizabilities including relativistic effects will be presented.



Figure 1: Scheme of two-photon absorption

Atomic relaxation and vibrational modes in quantum Monte Carlo

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ABSTRACT: Quantum Monte Carlo methods have become a leading contender for high accuracy calculations for the electronic structure. Calculating energy derivatives such as atomic forces and the matrix of force constants is important in relaxing structures, calculating vibrational properties, and performing molecular dynamics simulations. We develop a quantum mechanical expectation value to evaluate the matrix of force constants directly in Quantum Monte Carlo. The approach allows the full modeling of non-covalent bonds such as Van der Waals force, opening new applications to molecules and solids in condensed matter.

Highly-Accurate Equilibrium Structure of the C2h symmetric N1-to-O2 Hydrogen-bonded Uracil Dimer.

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Wavefunction-based composite-gradient approaches are able to obtain highly accurate *ab inito* structures at reasonable costs, competing with experimental structure determination methods.[1]

This presents the to-date most accurate geometrical parameters for the lowest-energy hydrogen bonded dimer of uracil.[2] This presents one of the largest CCSD(T)-based optimization done today. The choice of composite gradient is general and usuable in routine work on structural studies on biochemical building blocks.

We study bond elongations and contraction with respect to the monomer structure and discuss the impact of the structural change on interaction energy of the dimer, comparing to older high-level calculations. A new CCSD(T)-F12 based interaction energy is proposed.

We furthermore compare structural parameters with commonly used methods in the literature, such as several DFT flavors, among them the recent SCAN and B97M-X functionals, the double-hybrid B2PLYP-D3 and MP2/CBS itself. This allows a better judgment of the structural accuracy of DFT for larger biomolecules.

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Ultrafast spin-flip dynamics in transition metal complexes triggered by soft X-ray light

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Recent advances in attosecond spectroscopy open the door to understanding the correlated motion of valence and core electrons on their intrinsic timescales. For valence excitations, processes related to the electron spin are usually driven by nuclear motion. When going, however, to the core-excited states where the core hole has a nonzero angular momentum, a strong spin-orbit coupling starts to play a role [1-3]. In this work, we present a theoretical simulation of an ultrafast spin-flip dynamics driven solely by spin-orbit coupling and electron correlation in the L-edge $(2p\rightarrow 3d)$ excited states of a prototypical Fe(II) complex, which occurs faster than the core hole lifetime (about 4 fs) [4,5]. The non-equilibrium electron dynamics is studied by means of time-dependent restricted active space configuration interaction recast in the form of reduced density matrix propagation. The spin-orbit coupling atomic mean-field integral approximation. Dissipative effects of electronic and vibrational origin are considered as well. A detailed analysis of such phenomena will help to gain a fundamental understanding of spin-crossover processes and build up the basis for their control by light.

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Molecular simulation of the temperature dependence of the mechanical unfolding of a supramolecular complex

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The conformational dynamics of biomolecules and supramolecular complexes can be studied on a single molecule level using the techniques of dynamic force spectroscopy and important kinetic information can be extracted [1]. Using models for the free energy landscape of the system as a function of the molecular extension it is possible to obtain parameters like the bare unfolding rate, the activation free energy in the force-free case and also the distance between the folded configuration and the transition state. In the present work we performed molecular simulations of the mechanical unfolding of a model molecular complex, a pair of interlocked calixarene catenanes [3]. From rupture force distributions the kinetic rates for the opening transition were extacted for varying parameters of the pulling device. In order to be able to perform a model-free analysis we performed simulations over a broad range of temperatures and found Arrhenius behavior for the kinetic rates, cf. Fig.1. This allows to determine the activation free energy and the bare rate independently as a function of the force without using specific models for the shape of the energy landscape.



Fig.1: Kinetic rates obtained from temperature dependent force probe molecular dynamics simulations. Left: Rates for two temperatures obtained for various pulling velocities; Right: Arrhenius plots for different fixed values of the force (i.e. vertical cuts in the left panel)

In particular, we find an unphysically small distance between the free energy well and the barrier and a rather strong force dependence of the prefactor of the Arrhenius expression. We discuss our findings in light of the models that are usually used in the analysis of force dependent kinetic rates obtained from experimental or simulation data.

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Ab Initio View on the Interaction of Glyphosate with Soil Components

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For many years, the most widely used herbicide in the world "glyphosate" (GLP) was considered harmless to humans and the environment. It was commonly accepted that GLP is strongly bound to soil and therefore can not be easily leached into the environment. However, nowadays there is an ongoing GLP debate in view of its possible carcinogenic effects and its occurrence in ground and surface water. To understand reactivity and transport of GLP from soil to ground and surface water, we have conducted a series of joint experimental and quantum chemical studies to explore the nature and strength of the interaction of GLP with soil organic matter (SOM), soil minerals, free metal ions, and water (see figure) [1-3]. To accommodate the heterogeneity of soil, a SOM test set has been developed in terms of essential functional



building blocks [4]. The DFT results showed that GLP can interact strongly with the polar SOM building blocks via H-bond (HBs) formation and H-transfer. In contrast, GLP interacts weakly through dispersion interaction

with the non-polar SOM building blocks. Moreover, the GLP-SOM-interaction mechanism indicates to the importance of the polarity, explored electron density, and site of attack of the SOM fragments. Regarding soil minerals, periodic DFT based MD simulations are applied to explore possible binding mechanisms for GLP with different goethite surface planes in the presence of water. Here, a very strong interaction has been observed, involving covalent bond formation between GLP and goethite. Moreover, intramolecular HBs in GLP as well as intermolecular HBs between GLP and water, GLP and goethite, and water and goethite are found. Finally, the stability of complexes between GLP and a series of free metal ions has been explored. In conclusion, the multitude of binding mechanisms to soil components as well as to water make the occurrence of free GLP rather unlikely. But leaching of soluble GLP complexes with metal ions and small SOM fragments via preferential flow paths into waterways are rather likely.

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Magnetically induced electric currents in molecules with unusual topologies

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Qualitative rules for the describing the aromaticity or antiaromaticity and hence magnetically induced electric currents in planar or Möbius-twisted molecules have been known for over 50 years.¹ However, no rules are known for general surfaces or the influence of the geometry for molecules with a given topology.

We are using the gauge including magnetically induced current (GIMIC) method² to explore the electric currents in a number of molecular model systems. We employ all-trans-[40]-annulene as a physical realisation of a closed twisted ribbon and explore the effect of different degrees of twist and geometries of those ribbons on the induced electrical current strength.³ Toroidal surfaces are investigated at the examples of polyhex-carbon nanotori and nanotori that contain pentagon and heptagon faces.⁴ Toroidal surfaces may sustain helical currents that give rise to anapole moments.

This study not only serves a more complete understanding of the electronic structure of molecules with non-standard topologies but has potential applications as for example very large para-/diatropic current strengths or the switching of magnetic properties through deformation of molecular systems.

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Solvation and Mobility of Carbon Dioxide in Aqueous Alkanolamines: a Molecular Dynamics Study

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Reversible chemical absorption in amine solutions is considered as the most developed and promising technique for CO_2 capture from flue gas [1]. Further optimization of CO_2 capture processes, including design of new absorbers, requires entire understanding of molecular mechanism of CO_2 absorption. Molecular simulation methods can greatly contribute for solutions of such problems [2]. In the current work, we have performed molecular dynamics simulations of CO_2 solvated in alkanolamine/water mixtures at various solvent ratios for temperature range of 298-323 K. Four alkanolamine molecules have been selected for our study: monoethanolamine (MEA) as a standard, and 3-aminopropanol (MPA), 2-methylaminoethanol (MMEA), 4-diethylamino-2-butanol (DEAB) as potential novel CO_2 absorptive solvents.

Simulation results for aqueous MEA, MPA and MMEA are very similar. CO₂ molecules do not show any clear preferences to be located next to alkanolamines in comparison to locations near water, except for the case of the 80/20 (w/w) alkanolamine/water, at which water molecules are organized in small isolated clusters [3]. At increase of water concentration, relative presence of CO2 around alkanolamines slightly decreases. It happens because water displaces CO₂ molecules from positions near polar groups of alkanolamines. Another behavior has been observed for the case of DEAB. CO_2 molecules solvated in aqueous DEAB position themselves within clusters of DEAB molecules and avoid water. At increase of water concentration, relative presence of CO_2 around DEAB molecules increases, except the case of the 7.5/92.5 (w/w) DEAB/water. At this water-rich mixture composition water substitutes CO₂ from immediate positions at nitrogen atoms of DEAB. Diffusion coefficients from simulations are in good agreement with available for MEA and DEAB cases experimental results. Dependence of CO₂ diffusion coefficients on mixture compositions for aqueous MEA, MPA and MAE correlates with mobility of these alkanolamines in water [3]. Mobility of CO₂ molecules has been also described by a characteristic residence time during which a CO₂ molecule resides next to an alkanolamine molecule. Two-exponential decays of the residence correlation functions reveal two decay modes with long (about 10 ns) and short (less than 1 ns) residence times.

The obtained results are a first step for process-scale simulation and provide important qualitative and quantitative information for the design and engineering of new efficient CO_2 removal processes.

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SHARC Photodynamics of the TRANS-[RuCl(NO)Py4]²⁺

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Ruthenium nitrosyl complexes have found utility in a variety of applications, such as optical switches, data storage, and medicine. Depending on the ancillary ligands, environment, and irradiation wavelength, these complexes can undergo either intramolecular NO linkage photoisomerization or NO photorelease (Figure 1). In the past years, DFT studies of both the NO linkage photoisomerization and photorelease process in the trans-[RuCl(NO) (py)₄]²⁺complex revealed a complex two-step photoisomerization mechanism involving a sequential two-photon absorption.[1,2] This mechanistic picture has been confirmed experimentally recently.[3] The DFT study was based on the exploration of the lowest singlet and triplet potential energy surfaces, assuming efficient decay via intersystem crossing (ISC) from the first singlet excited state to the lowest triplet state. A further ab initio CASSCF/CASPT2 study[4] has supported and completed the DFT and experimental findings. In particular, the spin-orbit coupling outcomes helped to uncover the first steps of the photoisomerization process, suggesting an efficient singlet to triplet intersystem crossing after light absorption. At the same time, the topology of the CASPT2 potential energy surfaces highlighted the possibility of several photoisomerization pathways. It would be desirable to verify these hypotheses, by determining the most probable pathways. In this context, the surface hopping dynamics including arbitrary couplings (SHARC) method[5] represent a useful analytic tool to better understand the photochemistry of this system. Thus, in my presentation, I will present the results of the full dimensional surface hopping SHARC dynamics on the trans-[RuPy₄ClNO]²⁺ including non adiabatic and spin-orbit couplings, that describe: i) the role of the singlet and triplet excited states ii) the branching ratio between the different photoisomerization pathways iii) the most important quenching funnels that slow down the entire $N \rightarrow O$ isomerization process.



Figure 1. Photoisomerization and photorelease processes of a ruthenium nitrosyl complex

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The tardy dance of molecular orbitals

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Molecular orbitals are the basis for the understanding of chemical reactions. A positive interaction of orbital lobes with the same sign leads to the formation of covalent bonds. Car-Parrinello molecular dynamics (CPMD) simulations represent a unique tool to simulate such reactions. However, caution is advised: Movies of the motion of the molecular orbitals of benzene and cyclobutadiene show, how during such a dynamics run, the orbitals of the σ and π systems may rotate into each other leading to new linear combinations. The total density which can be computed as the sum of the single orbital densities, is unchanged by these rotations. As we show from the dimerization of cyclobutadiene, the predictability of chemical reactions is preserved. It is always possible to find one or several orbitals which reflect the chemical change. The rotations observed are not unique to Car-Parrinello molecular dynamics and are also seen in Born-Oppenheimer molecular dynamics simulations. Cyclobutadiene is shown to have a fluxional structure in contrast to benzene.



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Isotope effects by the infinite improbability drive

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Volatile organic compounds (VOCs) have been the focus of attention in the last decade, due to their recognition as potential pollutants and harm to the environment and humans. Isotopic fractionation via evaporation, has been used as a tool to provide vital information about stages, conditions, and pathways within such contaminants diffuse throughout ecosystems. In spite of the experimental data, there is a lack of theoretical models/tools that could provide insight to the ongoing phenomena.



Figure 1: Mean carbon VPIE for BB (left) and mean effective converged energy for bromine (BB) as a function of imaginary slices (right).

Vapour pressure isotope effects (VPIEs) for evaporation of bromobenzene (BB, C_6H_5Br), dibromomethane (DBM, CH_2Br_2), and ethanol (ETH, C_2H_5OH) were predicted using path integral (PI) formulation. In the case of BB and DBM, VPIEs were additionally calculated using QM/MM and QM cluster approach. PI, QM/MM and QM cluster results were compared to experimental data obtained for those systems. In general, cluster simulations tend to provide better results than PI and QM/MM models. Therefore, the hypothesis that QM cluster exhibit better results due to possible electronic structure changes that PI is unable to reproduce has been explored. Energy decomposition analysis (EDAs) on optimised dimers at the MP2/aug-cc-pVTZ level of theory reveals that for BB and DBM the main contributing force is dispersion, whereas for ETH electrostatics is as vital as dispersion. Recommendations, regarding what kind of subsequent approaches, as well as PI strategies ought to be followed (*ab-initio* PI and/or higher order PI) are given. National Science Center in Poland (Sonata BIS grant UMO-2014/14/E/ST4/00041) and in part PLGrid Infrastructure (Poland) have supported this work.

Electronic and Structural Properties along the Liquid-Vapor Coexistence Curve and in the Supercritical Phase of Water

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Supercritical fluids are substances above their particular liquid-vapor critical point (CP). According to standard textbook knowledge, the supercritical phase is homogeneous although it was shown that its structural and dynamical properties change dramatically upon varying the density [1, 2]. Especially in the case of water the continuously changing fundamental physical and chemical properties in its supercritical phase have been extensively exploited [3]. In this work we map the liquid-vapor phase diagram by ab initio Gibbs Ensemble Monte Carlo simulations using Density-Functional Theory with the RPBE functional, D3 dispersion corrections and employing the cp2k program code. Furthermore two state points deep in supercritical water (SCW) at 750 K and densities of 0.1 kg L^{-1} (low-density, LD-SCW) and 0.6 kg L^{-1} (high-density, HD-SCW) were simulated within the canonical ensemble using the same computational setup. [4]

Our results show that the CP according to the RPBE-D3 description overestimates the experimental one by 60 K whereas the critical density compares very well. The HD-SCW state consists of a mixture of large clusters surrounded by monomers and dimers whereas LD-SCW features clusters up to a maximum of 20 molecules but is vastly dominated by monomers and dimers. The overall structure is therefore fundamentally different at the two state points. Along the liquid branch of the coexistence curve the average number of H-bonds and the average cluster size decreases systematically when moving toward the CP from below. In contrast, the opposite is the case for the vapor branch: The density increases and therefore also the average number of H-bonds per molecule and the average cluster size increases. Regarding the electronic properties we show that polarization / charge-transfer effects decrease systematically along the liquid branch of the coexistence curve and are reduced by approximately 50 and 80 % in HD- and LD-SCW, respectively, compared to liquid ambient water. This explains fundamentally why THz spectra of SCW can be rather reliably computed using non-polarizable force fields [5], in stark contrast to ambient water.

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Computational Studies on NHC-Ligands on Metal Surfaces

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N-heterocyclic carbenes (NHCs) have emerged as valuable ligands for the functionalization of metal surfaces [1, 2]. Such modified surfaces show enhanced stability compared to their thiol-modified equivalents [3, 4] and were successfully utilized in biosensing [5] and catalysis [6, 7]. Despite advances in recent years, the influence of the NHCs' molecular structure on the interactions with the metal surface requires further investigation in order to access the full potential of applications [4, 8]. Density functional theory (DFT) is a powerful tool to characterize and design new materials [9, 10], which has already provided important insights into the interactions between NHCs and surfaces [3, 11-13]. However, periodic calculations featuring adsorbates on metal surfaces remain computationally demanding and users must choose a balance between the accuracy of the results and the time required to perform the calculations. Here, we present a thorough examination of the calculation setup for a model NHC on an Au(111) surface and compare results obtained with varying parameters such as distance between periodic images and slab size. These findings serve as guidelines to assess the cost/performance ratio in future calculations.

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Inverse Design of Dye Sensitizers and QSPR Model of DSSC

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How to find the highly efficient dyes used in dye sensitized solar cells(DSSC), is a significant and challenging task. To search all possible dyes by pure experimental researches is very cost- and time- consuming. To help solve the task, we applied our previous inverse design method[1][2] on porphyrin sensitizers and screen the most promising molecules out from a large pool of systems on the basis of our QSPR model. The inverse design method used "Gene Algorithm".

Different from our previous studies[2] to optimize benezene according to seperate optical properties (HOMO-LUMO gap, absorption, the overlap and spatial distribution of occupied molecule orbitals and unoccupied molecule orbitals, light harvest efficiency), now we optimized porphyrin according to solar cell efficiency(η). Moreover, the optical properties are the latent variables in the QSPR model to predict the observed variable η . The data library for QSPR model consists of 206 dye sensitizers, which are reported under similar experimental conditions in the literature and vary from porphyrin to small organic molecules.

Using our method, the program can directly output the molecule structures of promising porphyrin dyes. In addition, we found that some substitutes appeared often in the promising dyes. In the future, the promising dyes will be synthesized and tested the performance in solar cells.

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Heavy main group element – π interactions

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Heavier pnictogen $\cdots \pi$ arene interactions have received increasing attention in the last years.^[1-3] Many experimental and computational studies have been performed to unravel the nature of this intermolecular interaction. Pnictogen $\cdots \pi$ arene interactions are mainly dispersive in nature due to the high polarizability of the pnictogen atom, which makes them especially interesting in designing new supramolecular structures.^[4, 5]

In this study, the detailed computational analysis of the pnictogen $\cdots \pi$ arene interaction is presented. For this purpose, benzene and MR₃ molecules where M = As, Sb, or Bi and R = CH₃, OCH₃, or Cl were chosen as model compounds. Several methods including DFT-D, DFT-SAPT, MP2, and high-level coupled cluster methods in the DLPNO-CCSD(T) approximation were benchmarked to examine pnictogen $\cdots \pi$ arene interactions in model compounds.^[6] A novel energy decomposition scheme, the local energy decomposition (LED),^[7, 8] was used to investigate the dispersion energy contribution to the interaction energy and donor-acceptor properties of intermolecular interactions in MR₃-benzene adducts. Additionally, influence of the substitution (R = CF₃, NO₂, OCOH, OH, NH₂) in the benzene ring on the donor-acceptor properties in BiCl₃ and Bi(CH₃)₃ adducts were also studied by means of DFT-D and DLPNO-CCSD(T) LED methods.

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Non-orthogonal Product Wave Function Approach for Electron Transfer Integrals

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A key ingredient for the theoretical investigation of molecular electronics is the treatment of intermolecular electron transfer. The charge-transfer (CT) integrals occuring in the theory here are of additional interest for the CT-mediated pathway in singlet fission[1].

We describe the electron transfer process within a non-orthogonal product wave function approach. Electronic coupling coefficients in two- or multi-state systems are obtained by a Löwdin orthogonalization procedure[2].

Such a treatment of non-orthogonal wave functions has found renewed interest in e.g. nonorthogonal configuration interaction (see for example ref. [3]), and has been applied in the calculation of electronic coupling coefficients using different levels of theory (e.g. [4, 5]). Here we present our efficient approach based on individually selected determinants of the building blocks, compare its performance to other approaches and apply it to singlet hetero fission.

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Improving the description of the graphene-water interaction: A new electronic-structure-based force field

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The number of fascinating properties and incredible applications of graphene increases every year, thus attracting more and more attention [1]. Many of them, such as water purification [2] or energy storage [1], take place in aqueous media. Nevertheless, describing the interaction between water and graphene both, efficiently and accurately is still open to improvements.

Experimentally, there is an ongoing controversy about the value of the contact angle between water droplets and graphene, being the usual measurement to characterize the interaction between a surface and a liquid. The different measurements range from about 40 to 98° according to recent literature [3]. On the other hand, electronic structure calculations of graphene-water systems are troublesome due the graphene sheet size effects and the origin of this interaction, van der Waals forces. For this reason, only a few high-level calculations involving a single water monomer on graphene are reported [4]. In consequence, force field interaction models available in literature [5, 6] are debatable because they are based on controversial contact angle values [6] or on static *ab initio* results [5], where the contribution of other water molecules are avoided.

For this reason, in this work, a new water-graphene force field based on RPBE-D3 simulations is presented. RPBE-D3 is a computationally very affordable density functional that has been shown recently to describe many properties of water and aqueous solutions accurately. In the present case, we demonstrate that the RPBE-D3 description of the water/graphene interaction is in satisfactory agreement with previous CCSD(T) results [4] when benchmarked at the single molecule level. We show how our new force field can reproduce accurately the particle densities and hydrogen-bonding properties of the water/graphene interface obtained from explicit *ab initio* molecular dynamics simulations. The force field opens the possibility to compute slowly-converging properties, both in time and space, using force field molecular dynamics in conjunction with a suitable water model and allows us to estimate the contact angle. Moreover, the force field can be used in the framework of QM/MM simulations to exclude graphene from the electronic structure treatment, thus reducing the computational cost significantly.



Figure 1: Representative snapshot sampled from a water/graphene interface simulation.

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Automated Property Calculation for Fundamental Physics Tests with Molecules

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For many experiments that aim to test fundamental physics and in particular limits of the Standard Model of particle physics molecules and thus quantum chemistry play an important role. Interpretation of these experiments requires knowledge of molecular expectation values or transition matrix elements of a wide variety of symmetry violating operators. In the theoretical description of these properties relativistic effects typically play a major role. For many purposes it is not necessary to perform four-component relativistic calculations and quasi-relativistic twocomponent methods suffice, however, even in case of purely relativistic effects, as we have shown for molecular enhancements of a hypothetical electric dipole moment of the electron (eEDM).[1]

Many programs are designed for two-component calculations. Nonetheless the majority of twocomponent programs is restricted to the calculation of common molecular properties, such as NMR-shielding 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 more exotic, nonstandard properties, such as parity violating energy shifts or other customized 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 has great potential use.

In this poster a general formulation of relativistic one-electron properties in terms of density functions is introduced, which allows for automated code generation of a generic twocomponent 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 presented. The flexibility of the program is demonstrated by calculation of symmetry violating properties which are of importance for different fundamental physics tests, as well as by calculation of conventional hyperfine coupling and NMR shielding tensors.

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Interplay between Surface and Bulk Properties of Crystals

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Recently¹, we have demonstrated that, for any real material, there is a delicate interplay whereby the concerted interactions between all surfaces and the bulk region will influence the properties of the individual surfaces. Moreover, in some cases, these interactions will also affect the bulk properties. Thus, the requirement that no atom in the bulk shall experience a force from charges associated with the surface, a requirement we formulate in terms of a generalized Tasker condition², leads to an interplay between the charge densities of different surfaces for a given sample. Thereby, we also demonstrate that so-called polar surfaces that often are considered as unstable essentially always can be stabilized, although the details of this stabilization then depend on all surfaces of the sample, i.e., on the shape of the material. The consequences of this interplay are studied through one property that usually is considered a bulk property, i.e., the polarization/dipole moment per volume, and one property that usually is related to surfaces, i.e., the activity of a surface in heterogenous catalysis. Our theoretical findings are illustrated through results of density-functional and model calculations that are demonstrated to provide useful information.

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Molecular energy level matching to design model systems for singlet heterofission

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The process of singlet fission [1, 2] is of high interest in experimental and theoretical studies, as this bi-exciton generation can enhance the conversion efficiencies in photo voltaic cells. By generation of two triplet excitons from one singlet exciton the Shockley-Queisser limit can be overcome. Therefore experimental and theoretical investigations aim to understand the singlet fission process and to design new model systems with better singlet fission rate. The process can be described by the following simplified scheme:

$$S_1 + S_0 \rightleftharpoons {}^1(TT) \rightleftharpoons T_1 + T_1$$

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 a high singlet fission rate. 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 accomplished.

$$E(S_1) \ge 2 E(T_1)$$

 $E(T_2) > 2 E(T_1)$

Instead of singlet homofission, which takes place in the bulk of a molecular crystal like pentacene and generates twice the same triplet excition, this study focuses on singlet heterofission. This process is an interface specific correlation phenomenon, where two different molecules are involved. Here we discuss energy level matching to find potential candidate systems for singlet heterofission at interfaces.

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Surface phase diagram prediction from a minimal number of DFT calculations

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Adsorption on semiconductor and metal oxide surfaces is important for materials synthesis, sensors, and heterogeneous catalysis. Here, we show that adsorption of Cu atoms [1,2], small Cu clusters [3], water [4], and hydrogen [5] onto ZnO surfaces sometimes leads to electron donation from the adsorbate to the substrate, resulting in the ZnO conduction band becoming populated ("filled").

This band-filling has important consequences for the coverage dependence of adsorption energies in periodic DFT calculations. By employing the *band-filling correction*, which is commonly used for calculating defect formation energies in bulk semiconductors [6,7], it is possible to estimate also the adsorption energy in the low-coverage limit from a finite-coverage calculation [2-5] (Figure 1). Moreover, we show how the band-filling correction can be used to estimate the entire surface phase diagram for H₂ adsorption on ZnO from only four DFT calculations [5] (Figure 2).



Figure 1. Coverage dependence of adsorption energies for Cu atoms on ZnO.

Figure 2. Surface phase diagram for H adsorption on ZnO predicted from only four DFT calculations. $\Delta \mu_{\text{H}} = H$ chemical potential, $\theta = \text{coverage}, \ \theta^{\text{excess}} = \text{relative coverage of H@O and H@Zn.}$

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Enhanced O₂ activation caused by direct contact to the perimeter of Au/TiO₂ nanocatalyst

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Highly dispersed gold nanoparticles supported by reducible oxides such as titania (TiO₂) are able to catalyze a number of important reactions, including partial oxidation of hydrocarbons, water gas shift reaction, low-temperature CO oxidation, and selective alcohol oxidation via molecular oxygen [1]. Especially in reactions of the later type, the catalytic activation of the O_2 molecule is of major importance since it provides the oxidizing reagent.

The activation of the oxygen molecule has been shown to happen at active sites directly at the Au/TiO_2 interface, the so-called perimeter sites [2], in the realm of usual heterogeneous catalysis where the catalyst is in contact with the gas phase. In particular, a charge transfer mechanism has been proposed based on a set of static structure optimizations [2, 3]. Moreover, the provided electrons have been predicted to stem from the reduced oxide support, where excess electrons are localized at distinct Ti^{3+} sites. More recently, an accelerated *ab initio* MD study at finite temperature confirmed a charge transfer mechanism for the overall alcohol oxidation process in the presence of a gas phase [4]. However, the actual activation of the O₂ molecule and the explanation of the catalytic activity of the celebrated perimeter sites at the Au/TiO₂ interface are to be revealed.

Here, we present an *ab initio* thermodynamic integration study at elevated temperature of the O_2 activation which takes thermal fluctuation effects into account. We consider the O_2 species adsorbed directly at the Au/TiO₂ perimeter and far from the gold cluster at a free TiO₂ adsorption site serving as the internal reference state. The enhanced activation due to direct (perimeter site) contact of oxygen to the gold nanocatalyst is explained *via* in depth electronic structure analyses of representative snapshot configurations from the underlying *ab initio* MD trajectories.

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Non-covalent interactions as a guiding principle in the enantioselective alkynylation of α-ketoesters via copper catalysis

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Directionalyzed hydrogen bonds often play a key role in stabilizing not only intermediates and products, but also transition states. Thus, they are a very important element in developing new catalysts for asymmetric synthesis.[1]

Copper-catalyzed asymmetric direct alkynylation of α -ketoesters with terminal alkynes and with chiral prolinol-phosphine ligands afford various enantioenriched chiral propargylic tertiary alcohols.

Quantum-chemical calculations using the BP86 density functional including Grimme's empirical dispersion correction[2] show the occurrence of $OH\cdots O/sp^3$ - $CH\cdots O$ two-point hydrogen bonding between the chiral ligand and the carbonyl group of the ketoester in the stereodetermining transition states. Combined with the hydrogen-bonding interactions orienting the ketoester substrate, dispersive attractions between the chiral ligand (*P*-cyclohexyl groups) and the ketoester in the favored transition states, rather than steric repulsions in the disfavored transition state explain the enantioselectivity of the asymmetric copper catalysis.[3]



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Microsolvation of the Water Molecule and Hydronium by Bosonic Helium

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Studying the superfluidity of bosonic helium, ⁴He, has been a recurrent research field as it is a macroscopic manifestation of quantum mechanics and numerous studies have been carried out for superfluid clusters, some of them including molecular impurities. For theoretical studies of superfluidity path integral simulations are a widespread method. In that approach to quantum mechanics, each particle can be rigorously understood as a polymer of *M* beads in the $M \to \infty$ limit and this transformation is the basis of the isomorphism with a classical simulation of polymers which allows one to perform quantum calculations with essentially *M*-linearly increasing cost of classical mechanics. It is also possible to represent the exchange of indistinguishable particles by the connectivity of the polymers, necessary for the study of superfluidity of ⁴He systems.

In this work, microsolvation complexes of a water molecule and an hydronium cation with one to 12 ⁴He atoms at a temperature of T = 0.5 K are studied using a path integral Monte Carlo code, PIMC-MoRiBS [1]. This code is specific for calculations of a rigid molecular rotors in bosonic solvents where the rotational degrees of freedom of the molecular rotor are explicitly quantized. With this approach, the behavior of energetic and structural properties, as well as the superfluid responses of H₂O and H₃O⁺ are studied as a function of the number of helium atoms. Striking differences in these properties between these two simple molecules are disclosed.



- Figure 1: Hydronium ion microsolvated with nine helium atoms at a temperature of 0.5 K as represented by a single path integral snapshot configuration consisting of M = 512 beads.
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Development of a Neural Network Potential for Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are porous crystalline materials with many applications, from gas separation to heterogeneous catalysis. They consist of inorganic metal-oxo secondary building units, which are connected by organic linker molecules to form three-dimensional cage structures. By choosing these components, the chemical and physical properties of MOFs can be modified in a controlled way to improve the performance in these applications. To date, computer simulations of chemical processes in MOFs are severely hampered by the use of classical force fields, which in most cases are unable to describe the making and breaking of bonds, while the direct use of electronic structure calculations in ab initio molecular dynamics (MD) is computationally too demanding as often very large unit cells need to be considered.

Here we investigate the applicability of high-dimensional neural network potentials (NNP) to represent the density-functional theory (DFT) potential-energy surfaces of a series of crystalline MOFs using IRMOF-1, -10 and -16 as benchmark systems. In general, NNPs are an important class of machine learning potentials, which has been demonstrated to provide potential-energy surfaces with first-principles accuracy at the cost of simple empirical potentials for a wide range of systems. The training data for the NNP contains only the energies and forces of small molecular fragments cut from the periodic MOF structures. After a description of the method, we provide first validation results and preliminary MD simulations for the different bulk structures. We find that, as has been shown for a series of other systems, that small subsystems can be used to construct a NNP for MOFs, which is applicable to much larger systems.



Figure 1: Crystal structures of a) IRMOF-1, b)IRMOF-10 and c) IRMOF-16.

A Neural Network Potential for Lithium Manganese Oxides

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The lithium manganese oxide spinel $\text{Li}_x \text{Mn}_2 \text{O}_4$, with 0 < x < 2, is a prominent example of cathode materials in lithium ion batteries offering advantages such as low costs and non-toxicity.^[1] Its electronic structure changes with the Li content while no major structural changes occur in the range from x = 0 to 1. This decoupling of the electronic and geometric structure enables systematic studies and allows gaining insights into the properties of this material as a function of its composition.

However, an accurate description of $\text{Li}_x \text{Mn}_2 \text{O}_4$ by first-principles methods like density functional theory is far from trivial due to its complex electronic structure, with a variety of closelying electronic and magnetic states. It has been found that the local density approximation as well as the generalised gradient approximation are unable to describe $\text{Li}_x \text{Mn}_2 \text{O}_4$ correctly.^[2] We performed an extensive benchmarking using the hybrid functionals PBE0, HSE06, and the recently developed local hybrid functional PBE0r,^[3] with the result that these functionals yield energetic, structural, electronic, and magnetic properties which are in good agreement with experimental measurements.

Apart from the electronic structure, a second challenge is the need for large systems to perform simulations for realistic structural models addressing for example the lithium diffusion process. Employing density functional theory directly in form of ab initio molecular dynamics is unfeasible because of the high costs. We overcome this problem by employing an efficient and accurate machine learning potential based on neural networks. This high-dimensional neural network potential^[4] combines the accuracy of first-principles calculations with the efficiency of empirical potentials.

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Experimental and Theoretical High Energy Resolution X-Ray Absorption Spectroscopy

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Copper containing enzymes are a prominent example for bio catalysts that enable electron transfer. Understanding complexes like these is of great interest for catalytic applications. Two very important factors are the geometry and electronic structure, which strongly depend on the oxidation state of the metal. Exact knowledge of involved mechanisms is essential for understanding these compounds. High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy (HERFD-XAS) provides information about local geometry and the local spin state, by reflecting the details of the lowest unoccupied states.^[1] In this study we investigated a Cu(I) complex in the gas and in the crystalline phase as well as a single complex in water solution.

High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy (HERFD-XAS) was used in conjunction with different computational approaches. The fact that x-ray absorption spectroscopy is independent of the state of aggregation is important to study the complexes in their natural environment (e.g. soluted in water). The HERFD-XANES approach was used instead of the conventional XANES because of the higher resolution.

Calculations were carried out with the CP2K program suite.^[2] A combination of Ab initio molecular dynamics (AIMD) and DFT calculated XAS spectra was used. The computational approach involved an expansion of the Kohn-Sham orbitals in Gaussians while the electron density was described by a plane wave approach.

The experimental spectrum shows no prepeak as expected for Cu(I) (d10) but several features in the edge which were already discussed elsewhere.^[3] This study mainly focused on approaches for calculating these spectra with periodic boundary conditions and in solution. The agreement is good for each individual approach but several distinct differences will be shown. One example for these differences is the intensity ratio of the features to one another. This intensity depends in some cases on the approach and clearly shows the influence of the kind of underlying transition (e.g. charge transfer).

We show that this computational approach is in good agreement with the experimental spectra up to high energies. This is often a shortcoming for other approaches because of the highly delocalized electron density for the high energy transitions.

It will also become clear that the most expensive and generally most valid approach might not always give the best results.

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$\label{eq:cu2} Cu_2 Zn Sn S_4 \ \text{Kesterite - phase stability under pressure, Cd-doping and Ag} \\ analogues$

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At ambient conditions, Cu_2ZnSnS_4 crystallizes in the tetragonal kesterite (KS) structure (space group $I\overline{4}$, Z=2, Fig. 1). This phase is structurally derived from the sphalerite/zincblende (ZB) structure.

Various other phases are discussed as high pressure modifications or reached with specific synthetic conditions. [1, 2] We simulated the pressure dependence of various suggested Cu₂ZnSnS₄ structures including disordered ones (e.g. kesterite, disordered kesterite, stannite and GeSb-type phases) at DFT level using the PBE functional. We conducted a volume scan which corresponds to a pressure range of 0-100 GPa. A Birch-Murnaghan Equation of State was fitted to the data and the enthalpies (H(P) = E + PV) have been calculated. Thereby we accurately reproduce the experimental observations, predicting the kesterite \rightarrow GeSb-type phase transition at 15 GPa. [3] Applying the HSE06 hybrid functional we predict that unlike the starting semi-conducting kesterite-type Cu₂ZnSnS₄ structure, the high-pressure GeSb-type phase shows metallic conductivity.

Optical properties in this material for solar energy conversion can be changed by various doping mechanisms, often in line with structural changes. In experiment Cd doping $(Cu_2Zn_{1-x}Cd_xSnS_4)$ leads to a structural change from the kesterite to the stannite phase (space group $I\bar{4}2m$, Z=2) for a Cd molfraction beyond x=0.375. We simulated both phases in a 2x2x1 super cell and included all possible substitution patterns within the super cell and optimized them fully at the PBE level. We pre-

Figure 1: Unit cell for the Cu_2ZnSnS_4 kesterite structure. Blue: Cu, pink: Zn, gray: Sn and yellow: S.

dict a KS-to-ST transition at x=0.52. The deviation to the experiment could be due to cationic disorder in the kesterite phase. Work is in progress introducing disorder in the KS phase to reveal the influence on the transition molfraction.

To reduce cationic disorder the corresponding Ag-compound (Ag_2ZnSnS_4) is used in the experiment, due to the larger ionic radius. We tested a small set of differently disordered KS phases in 2x2x1 super cells at the PBE level and compared them to their Cu₂ZnSnS₄ analogues. The stability of the disordered phases decreases with the number of Ag-Zn exchanges, whereas for the Copper analogue one fully disordered structure is nearly as stable as the fully ordered structure.

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Global optimization of alkali clusters: Application of a modified embedded atom method

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Alkali metal clusters have been the focus of many theoretical and experimental studies. Besides their technological relevance they are used as model systems to test theoretical methods and to gain a better understanding of metal clusters in general (examplarily see references [1-3]).

The identification of the most stable cluster geometries is essential for the subsequent investigation of properties. Here for the first time the six most stable structures of alkali clusters Li_N and Na_N (N = 2 - 150) have been determined. A modified embedded atom method (MEAM) [4] was used within an unbiased global optimization procedure. Initially the MEAM was used to calculate various properties of bulk alkali metals, including stability and phonon dispersion with reasonable agreement with other experimental and theoretical work [4]. Furthermore our application to the lithium and sodium dimer also gave results comparable to reported theoretical studies and experiments. Therefore it was expected to work also for larger cluster sizes. Moreover the MEAM allows many calculations in short time due to its semiempirical analytic equations. Therefore an unbiased global optimization can be performed considering many million calculations for one cluster size leading to an extensive examination of the potential hypersurfaces.

Our global optimization procedure includes two main steps. First alkali clusters are generated randomly in different arrangements und subsequently are optimized locally using the first derivative of the analytic equations. Several calculations, each considering millions of clusters are performed, analysed and the six energetic lowest isomers are kept. These are used as input structures for the automatized Aufbau-Abbau algorithm in step two. The six most stable clusters resulting from the "random calculations" and the Aufbau-Abbau process present the globally optimized structures. Comparison to available data of other studies confirms the applicability of the MEAM to alkali clusters.

Besides a subsequent comprehensive energetic and structural analysis, the calculation of thermodynamic and melting properties of the optimized clusters will be done in the near future.

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20-Electron Octacarbonyl Anion Complexes [TM(CO)8]⁻ (TM = Sc, Y, La)

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ABSTRACT: The 18-electron rule, which ascribes a particular stability to transitionmetal (TM) complexes where the metal possesses a $(n)s^2(n-1)d^{10}(n)p^6$ noble gas configuration, is a very useful tool in inorganic chemistry.¹ Here, we report quantum chemical calculations on the stable 20-electron carbonyl anion complexes of group-three metals $TM(CO)s^-$ (TM = Sc, Y, La).² The molecules have a cubic (O_h) equilibrium geometry and a singlet $({}^{1}A_{1g})$ electronic ground state. The 20-electron systems $TM(CO)s^-$ are energetically stable toward loss of one CO ligand yielding the 18-electron complexes $TM(CO)_7^-$ in the ${}^{1}A_1$ electronic ground state. There is one occupied valence molecular orbital with a_{2u} symmetry of $TM(CO)s^-$, which is formed only by ligand orbitals without a contribution from the metal AOs. The adducts $TM(CO)_8^-$ fulfill the 18-electron rule when one considers only those valence electrons, which occupy metal-ligand bonding orbitals. Further energy decomposition analysis using TM^- ((n)s⁰(n-1)d⁴) and (CO)₈ has the order Sc > Y > La and the attractive metal-CO interactions come mainly from covalent bonding, in which the dominant contribution is the $[TM]^- \rightarrow CO \pi$ backdonation.



Figure 1. (a) Optimized geometries of $[TM(CO)_8]^-$ with the bond lengths (in Å) for TM = Sc, Y, and La in regular, italics, and in parentheses, respectively. (b) Splitting of the valence orbitals of the metal and $(CO)_8$ in the cubic field of $TM(CO)_8^-$.

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QM/MM Dynamics to Study Excitation Energy Transfer in the FMO Light-Harvesting Complexes

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Green sulphur bacteria (GSB) harvest sunlight by absorbing photons through their large antenna complex known as chlorosomes and transfer this solar energy to a reaction center for photosynthetic charge separation. During this process, the excitation energy is absorbed by chlorosomes and passed through Fenna-Matthews-Olson (FMO) complexes to the respective reaction centers (RC) ^[1]. In recent years, the FMO complex has caught quite some attention especially due to the claim of experimentally observed long-lived quantum coherences. In the present study, we performed ab-initio QM/MM dynamics of the FMO complex to explore the excitation energy transfer among its bacteriochlorophyll pigments at room temperature. To this end, we have applied the self-consistent-charge Density-Functional based Tight-Binding (SCC-DFTB) technique to perform dynamical simulations together with the CHARMM force field in a QM/MM fashion^[2]. Subsequently, time-dependent long-range corrected Density-Functional based Tight-Binding (TD-LC-DFTB) calculations were performed along this QM/MM trajectory to determine the excitation energy fluctuations of each pigment ^[3]. In a next step, auto-correlation functions and spectral densities have been extracted from the energy gap fluctuations which can serve as input for density matrix calculations. Furthermore, the present investigations have been compared to semi-empirical ZINDO/S-CIS calculations along classical trajectories.

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Tuning Aromaticity of para-Substituted Benzene Derivatives

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For aromatic species, substituent effects are phenomena which strongly influence properties of these systems [1,2]. This leads to the question of the interrelation between aromaticity and substituent effect. This work examines changes in aromaticity in para-substituted benzene derivatives exposed to external electric fields of various intensities. Three systems: *para*-aminophenol, *para*-nitrobenzonitrile and *para*-nitrophenol with different substituent electron-accepting/donating properties are studied (for spatial orientation of these systems, see Figure).



Figure: Orientation of para-substituted benzene derivatives in an external electric field.

The interrelation between aromaticity and the substituent effect appears to be of a competitive nature [3]. The aromaticity of the benzene ring (and the substituent effect) in such systems can be tuned by changing the intensity of the external electric field [3]. Such tuning is most effective for a system containing one electron-donating and one electron-accepting substituent.

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Two-Dimensional Phosphorus Carbide Polymorphs: Influence of Structural Motifs on the Band Gap

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Since the discovery of graphene in 2004 and the subsequent Nobel prize in 2010 twodimensional (2D) materials became one of the most active fields in science. Graphene as cutting-edge material shows a lot of interesting properties, such as Dirac cones in combination with an extraordinarily high carrier mobility. However, the semimetallic nature of graphene impedes its applications in transistors and all attempts on opening a sizeable, robust band gap without losing the high carrier mobility failed so far.

In this contribution, we use ab initio DFT calculations to suggest stable polymorphs of twodimensional phosphorus carbide monolayers with the 1:1 stoichiometry (PC) to evaluate the potential of these compounds as highly mobile semiconductors for electronic circuitry [1,2]. For that purpose, their stability was verified by molecular dynamics simulations. Furthermore, the structural motifs could be linked to the electronic properties and therefore an explanation for the occurrence of a Dirac cone or band gap can be offered.



Figure 1: PC monolayer with highlighted primitive unit cell (left) and associated highest occupied crystal orbital (right). Phosphorus and carbon atoms are depicted in red and black respectively.

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Al and mixed Al/Fe Oxide Gas-Phase Ionic Clusters: Theoretical Investigation for Spectroscopy Experiments.

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A novel Al-oxide cluster was synthesized with the aim of trapping early intermediates during Al precursor hydrolysis.[1] The gas-phase anion, as depicted in figure 1, was probed with action Infra-red Spectroscopy (IR-PD). DFT models suggest that the (AlO)₃ core undergoes structural change upon ionization. Intramolecular interactions between the bridging OH groups and the aromatic ligand moieties influence the structure and the spectral features.

In a separate work, we investigate the suppression of Hydrogen Atom Transfer (HAT) reactivity by the replacement of one Al atom for Fe, as depicted in figure 2, in a small mixed oxide cluster cation. The cluster Al_8O_{12} + has a predicted structure which deviates from the bulk corundum structure.[2] Calculations predict high spin density on the apical oxygen, suggesting radical character. This explains the 'direct' HAT reactivity as observed with methane.[3] IR-PD data has been collected for the mono-substituted cluster FeAl₇O₁₂⁺. DFT was used to explain the low reactivity, assign the IR-PD spectrum and assess the Fe electronic structure.



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Modeling the pressure dependence of the hydrophobic effect of amyloids in aqueous solution

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The hydrophobic effect has strong influence on the folding behaviour of proteins. Most proteinogenic amino acids include hydrophobic residues. In the native state of the protein in water most hydrophilic groups are directes outwards to the aqueous environment, whereas the lipophilic residues point inwards.

The activity of insuline, for example, decreases strongly under abyssal conditions (below 1000 m depth). At the corresponding pressure, its tertiary structure changes significantly [1].

Some deseases of the human brain, e. g. the Alzheimer disease, are caused by proteins which cannot be disassembled due to their prion-like misfolded structure. It is the aim of this work to investigate the pressure dependence of the misfolding.

Due to the size of the molecule and its hydration shell, the preliminary calculations are carried out with molecular dynamics using the force field based code GROMACS[2]. Further calculations with higher accuracy are planned with the Car-Parrinello-code CPMD [3].

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Description of Intermolecular Charge-Transfer with Subsystem Density-Functional Theory

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Intermolecular charge-transfer plays an important role in organic photovoltaics [1]. However, the correct description of intermolecular charge-transfer with density-functional theory has proven to be difficult because of the self-interaction error (SIE) in approximate exchange-correlation functionals [2].

Here, we investigate a tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) model complex as a test case. We analyse the fractional charge error for this complex and find that the non-linearity of the monomer energies as a function of the total charge causes large errors in the derivative gap, which in turn leads to a negative HOMO-LUMO gap in the dimer.

To overcome this error we apply subsystem density-functional theory [3]. With this approach we partition the complex into two subsystems with opposite fractional charges and calculate the energy of the monomer subsystems and their interaction energy as a function of the fractional charge. For the monomer subsystems, we correct the fractional charge error by applying a linear interpolation between integer charges.

We find that subsystem density-functional theory overcomes the SIE and describes the chargetransfer correct. The transferred charge as a function of the electric field shows the expected integer electron jump.

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Systematic exploration of a reaction network by density functional theory: The growth of gallium phosphide on semiconductor surfaces

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A fundamental step for future technologies is the development of new semiconductors. Promising candidates belong to the group of III/V semiconductors which are commonly grown by metal-organic vapour phase epitaxy (MOVPE).

An atomistic model for the growth mechanism of for example gallium phosphide (GaP) is desirable but due to the high complexity of the surface chemistry yet inaccessible. The high number of surface reconstructions and the complexity of precursor molecules and their decomposition characteristics, which need to be considered in order to accurately understand and describe the underlying chemistry, require a systematic or even partially automated approach.

We are developing a systematic and hierarchical procedure to explore the reaction network including the adsorption, diffusion and decomposition of precursor molecules on a semiconductor surface.

The procedure follows a grid-based scheme to generate starting structures (figure 1) which are optimized by density functional theory in a periodic slab model. Unique minima are selected according to their energy and root-mean-square deviation to all other obtained structures. In a subsequent step, the minimum energy paths describing a diffusion or a decomposition are selected step-by-step with gradually increasing complexity and calculated by double ended methods (e.g. the nudged elastic band method).



Figure 1. A grid (blue spheres) is stretched above the surface ensuring a regular distribution of precursor molecules along the in-plane axes and a constant distance to the GaP(001) surface (left). Diffusion paths (dashed lines) connecting obtained minima (blue spheres) are proposed (right).

Simulation of High Harmonic Generation spectra for molecular isomers using the time-dependent Configuration Interaction Singles method

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When atoms or molecules are irradiated with short intense laser pulses, they can emit photons with frequencies that are integer multiples of the laser frequency - a process known as High Harmonic Generation (HHG) [1]. HHG spectra are closely related to the electronic structure of the investigated species. For instance, recently cis- and trans-1,2-dichloroethene (cis-1,2-DCE and trans-1,2-DCE, respectively) were experimentally distinguished by means of their HHG spectra [2]. In this contribution, we report computed HHG spectra for both molecular isomers using the time-dependent Configuration Interaction Singles (TD-CIS) method in an atom-centered basis [3]. When computing HHG spectra with this method, the choice of appropriate basis functions for the description of the electron's large-amplitude motion in the continuum is one of the most critical issues. Further, since HHG involves ionization and the molecules are randomly oriented, we use a heuristic model for ionization and perform rotational averaging [4]. We present a detailed analysis of the influence of the basis set and ionization on the HHG spectra for cis-and trans-1,2-DCE. The latter show qualitative agreement with the experimental spectra and differences between both isomers can be discussed on the basis of our calculations.

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Accurate vibronic quantum dynamics of NO₃ using a diabatic neural network potential

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The accurate theoretical treatment of nonadiabatic nuclear quantum dynamics requires the availability of accurate coupled potential energy surfaces (PESs). The development of such PES models is still an unsolved problem. Therefore, a new diabatization method based on artificial neural networks (ANNs) has been developed, which is capable to reproduce high-quality *ab initio* data with excellent accuracy. The diabatic potential matrix is expanded in terms of a set of basic coupling matrices and the expansion coefficients are made geometry-dependent by the output neurons of the ANN. The ANN is trained with respect to *ab initio* data using a modified Marquardt-Levenberg back-propagation algorithm.

This novel ANN diabatization approach has been applied to the low-lying electronic states of NO₃ as a prototypical and notoriously difficult Jahn-Teller system in which the accurate description of the very strong non-adiabatic coupling is of paramount importance. The newly developed diabatic ANN PES model reproduces a set of more than 90000 MR-SDCI energies for the five lowest PES sheets with an rms error well below 50 cm⁻¹. The vibronic spectra of the electronic ground state of ²A'₂ symmetry and the first excited state of ²E'' symmetry have been studied by accurate quantum dynamics calculations using the new model. The results show unprecedented agreement with high-resolution FT-IR spectra [1] and jet-cooled CRD spectra,[2] respectively, and greatly improve our previous studies.[3-4] The results are sufficiently accurate to pinpoint experimental misinterpretations unequivocally and hopefully will help to settle a longstanding dispute. These results also demonstrate the power of the newly developed method.

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Functionalization of MoS₂ with light switchable azobenzene

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The optical and electronic properties of multilayer molybdenum disulfide and other transition metal dichalcogenides crucially depend on the interlayer spacing and, in general, on the surrounding dielectric medium [1]. This motivated the idea to investigate layered two-dimensional materials which exploit the photoinduced isomerisation of covalently bound azobenzene to reversibly alter the system's properties.

The functionalization of MoS_2 with light switchable azobenzene is investigated by *ab initio* calculations. Sulfur vacancies are considered as reactive centers for thiol and amino groups to covalently bind. Density functional theory (DFT) is employed to analyse the stability of these configurations and to determine their electronic structure. The influence of the MoS_2 layers on the photoswitching mechanism and efficiency is studied using excited state ab initio molecular dynamics based on TDDFT. The band structure and the absorption spectrum of the 2D structures are treated within the many-body perturbation theory in the *GW* approximation using a perturbative LDA+GdW approach [2] to take polarization effects and inhomogeneous screening into account.



Figure 1: Two stable ground state geometries of MoS₂ layers linked by trans (left) and cis (right) azobenzene.

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Ab Initio Simulations of P-Compounds at Mineral Surfaces

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Phosphorus (P) plays an important role in the environmental nutrient cycle. P is central to all forms of life and its efficient use in fertilizers is one of the conditions for providing food for a rapidly increasing human population. Facing the projected peak P scenario, substantial research activities have been triggered to improve our knowledge towards a more efficient and sustainable use of P resources. One major factor playing a role in the P immobilization and thus efficiency is the strong interaction of phosphates to soil mineral surfaces and especially to Fe- and Al- oxyhydroxides. To draw a molecular level picture about this interaction, we have studied binding of two abundant phosphates (inositol-hexa phosphate (IHP) and glycerolphosphate (GP)) at two different mineral surfaces (goethite (FeOOH) and diaspore (AlOOH)). Here, water as an aqueous solution in soil was involved around each phosphate-mineral model. In the current contribution, all models are treated by DFT using periodic boundary conditions (PBC). The calculations are performed using the mixed Gaussian and plane wave approach implemented in CP2K. Due to size of our models, QM/MM calculations have been performed to have good accuracy with less computational time. Here, the relevant reactive molecular system including the top two layers of the mineral surface, phosphate, and the surrounding water molecules are described at QM level. During the MD simulations, different binding motifs including monodentate and bidentate are observed between the phosphates and the mineral surfaces. Moreover, protons transfer from phosphates to the mineral surfaces as well as to the surrounding water molecules. In addition, the interfacial water molecules interact with the mineral surfaces via formation of covalent bonds and H-bonds. Furthermore, dissociation of some water molecules is observed at the surface to protons and hydroxyl groups. More details will be presented in the poster.



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An extended Hamiltonian approach to adaptive QM/MM simulations

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QM/MM calculations can greatly reduce the computational cost by treating the chemically inert environment classically by molecular mechanics (MM) and the chemically active core by a quantum-mechanical (QM) method [1]. Thus they provide access to a wider range of phenomena occuring in extended systems, such as biomolecules. In many cases, the partitioning of the system into QM and MM regions needs to be redefined during the simulation, e.g. to guarantee a solvation shell of quantum-mechanical water around the active core at all times.

Instantaneous switching between interaction potentials, e.g. switching an atom or molecule from MM to QM treatment and vice versa, violates energy conservation. There have been a number of different approaches to adaptive QM/MM simulations relying on spatial partitioning schemes [2], but they still lack energy conservation. Here we proposed an adaptive QM/MM method based on an extended Hamiltonian approach recently developed for switching between different potentials in the time-domain [3]. As a proof-of-concept for the proposed method, we simulate an argon gas in which the interactions are modelled by a Lennard-Jones potential,

$$V = 4\epsilon_i \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right].$$

A potential energy surface V_1 is defined, where all atoms closer than a chosen threshold of 7 Å to a selected central atom are assigned $\epsilon_i = \epsilon_2$, all others $\epsilon_i = \epsilon_1$. For atomic interactions between ϵ_1 and ϵ_2 Lorentz-Berthelot rules are used with $\epsilon_i = \sqrt{\epsilon_1 \epsilon_2}$. When the atoms diffuse during the simulation the partitioning might change, thus defining a new potential energy landscape V_2 . In comparison to QM/MM switching the parameters have been chosen to simulate 20 % of energy difference between the interaction potentials. The extended Hamiltonian

$$H^{\text{ext}} = E_{\text{kin}} + \text{sgn}(\Delta V) \frac{p_{\lambda}^2}{2\mu} + \{g(\lambda)V_1 + [1 - g(\lambda)]V_2\}$$

yields coupled equations of motion, for the nuclei and a fictitious degree of freedom λ with an associated mass μ , which can be integrated by the velocity Verlet algorithm. $g(\lambda) \in [0, 1]$ is called the switching function and determines the relative weighting of the potentials V_1 and V_2 . In this work we discuss how the choice of the fictitious mass μ influences energy conservation and switching speed.

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Low-barrier hydrogen bonds in enzymes: a static or a dynamic concept?

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Allosteric regulation and cooperativity phenomena are ubiquitous in protein function. Many enzymes are known to change their activity in response to a chemical stimulus from the substrate itself. Binding of the latter to allosteric regulation sites or to the active site in enzymes can lead to a change of the global tertiary and quaternary structure. Recently, it was discovered that enzymes utilizing the vitamin B1 cofactor thiamin diphosphate (ThDP) such as e.g. pyruvate dehydrogenase feature a communication channel between the two remote active sites of the obligate functional dimers [1,2]. The atomic structures suggested that a 'proton wire' consisting of numerous acidic amino acid residues and water molecules synchronizes the catalytic events at the two active sites by reversibly shuttling a proton through this channel in a Grotthuss-type mechanism thereby chemically activating the bound cofactors in reciprocal manner [2]. In this work we focus on the human transketolase (pdb code: 4kxw) also a ThDP-dependent enzyme. X-ray diffraction experiments at an unprecedented 0.8 Å resolution identify a proton sitting in between two Glu residues (E366' and E160). Through the combination of molecular dynamics and quantum mechanics/molecular mechanics (OM/MM) calculations, we have found a viable mechanism of transport and are able to link the experimental assignment of the "proton density" to the latter pathway. The delocalization of the proton is confirmed by alchemical QM/MM runs, shifting the proton density in/out of an active site, and solving the proton wave function equation for the respective model potentials.

The system enables a unique opportunity for the study of the strongly disputed concept of low-barrier hydrogen bonds (LBHB). Our calculations show that such labile protons are better understood considering the dynamics of the full system, instead of regarding a single potential well for an individual hydrogen bond.

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Automated Active Space Selection for DMRG-SCF based on 2nd Order Perturbation Theory

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The Density Matrix Renormalization Group [1] (DMRG) algorithm has attracted significant attention as a robust and valuable quantum chemical approach to multi-reference electronic structure problems in which a large number of electrons are strongly correlated. It enables us to include large number of orbitals into the active space. Naturally, the selection of active orbitals is crucial in such calculations. We present an approach for selection of active space molecular orbitals for large scale DMRG-CI and DMRG-SCF calculations. Our approach involves a two-step procedure. A Strongly Contracted Variant of 2nd Order N-electron Valence State Perturbation Theory [2, 3] (SC-NEVPT2) calculation is performed on top of a CASSCF reference with a small active space, thus generating the First Order Interactive Space (FOIS). Internal and external parts of the FOIS density matrix are calculated and then diagonalized to obtain the quasi-natural orbitals. The choice of orbitals to be included in large active space is guided by the Natural Orbital Occupation Numbers (NOON). As we start with a wavefunction from a small active space calculation, this can be regarded as a "bottom-up" approach. We envisage the development of a reliable scheme for selecting larger number of unoccupied and occupied orbitals to include them into the DMRG active space.

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Modelling charge transport in bulk heterojunction organic solar cells by kinetic Monte Carlo simulations

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The theoretical study of charge transport in organic solar cells is a challenging task since it involves multiple time and length scales - from quantum-mechanical charge transfer processes at the molecular level to mesoscopic structural and dynamical parameters governing the morphology of the amorphous donor/acceptor material [1]. Our goal here is to compute the mobility of electrons and holes in a multiscale model via a kinetic Monte Carlo simulation using bimolecular charge transfer rates on the basis of Marcus theory. Therefore accurate hopping rates between neighboring molecules are mandatory, which depend on the internal and outer-sphere reorganization energies, charge transfer integrals, and external driving forces. These contributions to the hopping rates vary as a function of position and orientation of the molecules in the amorphous morphology. The intermolecular charge transfer integral for a given charge transfer complex is calculated with a projection method of the monomer orbitals on the dimer orbitals (dimer-projection method, DIPRO [2]), while the intramolecular transfer integrals are modeled with constrained density functional theory (CDFT)[3]. The atomistic morphology is partitioned into hopping sites. For a list of neighbour molecules, the coupling matrix element, the reorganization energy and the driving force are calculated. The hopping rates are then fed into the Monte Carlo simulations which allow us to monitor the charge dynamics in the system as well as to get ensemble averages of the occupation probability, charge carrier mobilities and correlation functions. A detailed knowledge about these quantities may help to enhance the performance of bulk heterojunction solar cells. Here we apply this approach to a recently proposed mixture of the DiPBI acceptor and the P3HT donor [4].

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Kohn Sham methods based on the adiabatic-connection fluctuation-dissipation theorem and powerseriesapproximations for the exchange-correlation kernel

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In recent years methods based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem for the computation of the Kohn-Sham correlation energy were explored. The ACFD theorem, in principle, yields the exact Kohn-Sham correlation energy. For the evaluation of the correlation energy via the ACFD theorem the density-density response function is needed. The calculation of this response function requires the unknown exchange-correlation kernel f_{Hxc} , the frequency dependent functional derivative of the exchange correlation potential. In the simplest case only the exactly known Hartree kernel f_H is taken into account and the exchangecorrelation kernel f_{xc} is neglected. This amounts to the direct random has approximation (dRPA) invastigated by various groups. In recent years we have developed a systematic hierarchy of approximations to go beyond the dRPA by taking into account the exact exchange kernel and by considering the correlation kernel via a power series approximation (PSA)[1-7]. Motivated by the success of a first PSA kernel [7] that contained contributions up to fourth order in the electron-electron interaction different infinite order PSA approximations are explored. The resulting new approaches proved to be quite versatile and are able to highly accurate describe electronic systems ranging from atoms and molecules to the homogeneous electron gas including situations chracterized by strong (static) correlation like dissociating molecules or Wigner cristallisation.

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Modeling Ionizations Using ADC

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The theoretical modeling of ionization processes and simulation of corresponding photoelectron spectra is a demanding task for quantum chemistry. With the Algebraic Diagrammatic Construction approximation for the electron propagator (IP-ADC), a successful approach to this problem has been developed[1]. Here, we show an efficient implementation of IP-ADC up to third order in adcman[2], a suite of ADC methods for electronically excited and ionized states, which is available through the Q- Chem quantum-chemical program package[3].

A second part of the poster focuses on resonant autoionization. As illustrated in Figure 1, such processes occur if an electronic system is excited above its ionization threshold. Due to the unbound nature of the involved resonance states, their theoretical description is challenging. An implementation of the Fano-ADC-Stieltjes method[4], which combines Fano-Stieltjes theory[5] with the Algebraic Diagrammatic Construction approximation for the polarization propagator (ADC)[6], is presented.



Figure 1: Schematic illustration of a resonant Auger process as an example for autoionization.

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Theoretical THz Spectroscopy of Aqueous Urea Solutions: From Ambient Conditions to High Hydrostatic Pressures

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Urea serves as a denaturant for proteins from biochemistry to biotechnology and is also found as a co-solvent and metabolite in living organisms. Yet, the molecular mechanism underlying unfolding of native proteins remains controversial. One hypothesis is that urea is disturbing the water structure such that it leads to a better solubility of hydrophobic groups, thus exposing the hydrophobic core of proteins, whereas other scenarios argue in favor of local protein-urea interactions. Surprisingly, there is a wealth of studies devoted to understanding protein-urea interactions, whereas the more fundamental urea-water interactions are rarely addressed. In this study, we therefore comprehensively analyze the solvation of urea in bulk water under ambient conditions and assess the changes that occur upon compression to 10 kbar using converged ab initio molecular dynamics simulations that rely on the RPBE-D3 density functional that has been carefully validated for aqueous solutions. Beyond a standard analysis of structure and dynamics, our particular focus is on the far-infrared/THz response, which directly probes the H-bond network at the urea-water interface, including pressure effects on the solvation pattern as probed by THz spectroscopy.

Materials Modelling, Multiscale Simulations and Global Optimization – new features in the CAST program package

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CAST (Conformational Analysis and Search Tool)^[1] contains efficient global optimization routines based on a combination of basin hopping and Tabu Search^[2-4], and reaction path search approaches which combine the Nudged Elastic Band (NEB) with the PathOpt^[5] approach. Additionally, CAST is able to perform MD and MC simulations as well as free energy perturbation calculations (FEP). By its modular conception, the implemented algorithms can be easily applied employing different energy-calculating methods ranging from different force fields up to fast DFT calculation with Terachem.

Recently, this modularity was expanded to include multiscale modelling approaches via common additive or subtractive electrostatic embedding schemes. Interfaces to the DFTB+, Psi4 and Gaussian software have been implemented, considerably widening the range of computational approaches.

To enhance the global optimization capabilities of CAST, the promising translation-rotationinternal coordinates (TRIC) of Wang and Song^[6] are included in the current development version. These coordinates are expected to accelerate convergence of optimizations. For the modelling of organic semiconductors devices, e.g. solar cells, the procedure of Brückner et al. is available^[7-8]. This protocol can generate atomic models of semiconductor devices comprising amorphous phases. The relevant processes in the bulk (exciton or charge diffusion) and at the interface (e.g. charge dissociation) are mimicked to evaluate the overall performance.

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Cost Effective Reaction Energies for Organic Reactions from "Exact" WF-in-DFT Embedding

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Describing the reaction energetics of large systems can be a demanding task for correlated wavefunction (WF) methods. Embedding approaches like WF-in-density functional theory (WF-in-DFT)[1, 2, 3] can help in reducing this cost. Exact embedding (within a DFT context) of the WF-method can be achieved using projection-based embedding (PbE) [4]. However, the computational cost of the embedded WF-calculation is only reduced significantly if PbE is used in combination with a basis set truncation scheme. [5, 6]



Fig. 1: Valine-proline-leucine tripeptide as an example molecule from the test set.

Fig. 2: DFT-in-DFT embedding error averaged over a representative set of test systems for the Def2-TZVPP basis set.

In this work the implementation of the Huzinaga projection operator [7], Hoffmann's projection operator [8] and the levelshift by Manby *et al.* [4] in our group's quantum chemistry program SERENITY [9] is reported and the operators are compared regarding their performance in a truncated basis set for DFT-in-DFT embedding, employing the scheme from Ref. [6]. Example calculations are presented for MP2-in-DFT embedding for reactions of organic molecules.

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Kinetic models of the Cyclosporines A and E

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Cyclic peptides have gained high interest as potential drug candidates. However, they often suffer from a low bioavailability due to their size and complexity. One exception is the undecamer Cyclosporine A (CsA), which can passively diffuse through the membrane. The reason for this is most likely found in its dynamic behavior as it can change between an "open" and a "closed" conformation. Cyclosporine E (CsE) is a synthetic derivative of CsA, missing a backbone methylation in Val-11. Its membrane permeability, however, is one order of magnitude smaller [1,2].

To get a better understanding of the dynamics of both molecules and their kinetic differences MD-simulations in water (polar solvent) and chloroform (apolar solvent) have been performed [1,2], which are analyzed using core-set Markov-State-Models (cs-MSMs). In cs-MSMs one focuses on the metastable states of the system, called core sets. This has the advantage that only a small number of states is needed to describe the dynamics accurately [3,4]. We showed that using this kind of analysis recrossing can be reduced and disconnection of metastable states within the data set can be pointed out. In addition, we analyzed the influence of the cis-trans isomerization of the 9-10 peptide bond, which seems to be an important factor for the conformational changes of CsA and CsE, and compared both molecules using a combined discretization.

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Benchmark and Application of LC-DFTB on Light-Harvesting Complexes

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Huge multichromophoric systems like light-harvesting complexes require a fast and thus accurate computational method to be discribed properly. Such a method is given now through the implementation of a long-range corrected functional into the DFTB approach. This allows for a sufficient sampling of excited state properties of these systems within the LC-TD-DFTB framework [1],[2]. We provide a benchmark study of the LC-DFTB method applied to the Bacteriochlorophyll a chromophore. Furthermore we present the application on light-harvesting complexes LH2 and LH3. Classical and QM/MM simulations were performed for sampling. To show the influence of structural changes, external fields and exciton coupling on excitation energies, absorption spectra for LH2 and LH3 are calculated.

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Ab initio calculations of the cohesive energy of the low temperature α phase of elemental F_2

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Elemental fluorine crystallizes as α -F₂ below 45 K in the monoclinic C/2c space group (see fig. 1a)[1]. This is in contrast to the the other halogens Cl₂, Br₂ and I₂ that all crystallize in the orthorhombic Cmca space group. Lacking a permanent dipole moment, α -F₂ binds through London dispersion interactions and σ -hole bonding, the latter contributing to the relatively high melting points of the heavier halogens.

The cohesive energy (E_{coh}) of α -F₂ has been calculated with dispersion-corrected DFT, local MP2 (both periodic) and CCSD(T) (incremental; cluster calculations[2]). In addition, a Cmca phase was optimized using local MP2 and compared to α -F₂ (see fig. 1b). Even with dispersion correction, DFT shows an underbinding of 17-58% depending on the functional. In contrast, both local MP2 and CCSD(T) pinpoint E_{coh} within sub-kJ/mol accuracy.

All methods correctly favor the C/2c phase. The difference in energy is in the order of 0.5 kJ/mol and attributed to a larger Pauli repulsion in Cmca, as seen in the Hartree-Fock calculations. From the CCSD(T) calculations we have confirmed that σ -hole bonding also occurs in F₂.



Figure 1: (a) Crystal structures of C/2c and Cmca represented as the nearest neighbors of a reference molecule. The plane marks the main structural difference: molecules aligned parallelly on top (Cmca) or slightly shifted (C/2c). (b) $E_{\rm coh}$ calculated with various methods for both phases. Dotted line: exp. value 8.4 kJ/mol[3].

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QM/MM studies of proton coupled electron transfer in ribonucleotide reductase

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Enzymatic active E. coli ribonucleotide reductase (RNR) composed of two homodimers, $\alpha 2$ and $\beta 2$, catalyzes the conversion of ribonucleotides to deoxyribonucleotides. Nucleotide reduction is induced by a long-range radical transfer from a stable diiron-tyrosyl radical (β -Y₁₂₂•) cofactor in subunit β to a cysteine (α -C₄₃₉) located over 35 Å away in the active site of subunit α [1]. Radical propagation is facilitated by sequential and reversible proton-coupled electron transfer (PCET) steps between several redox-active residues, mainly tyrosines, along a specific pathway. The initial PCET occurs in subunit β between cofactor tyrosyl β -Y₁₂₂• and β -Y₃₅₆ located at the $\alpha 2\beta 2$ interface, followed by three successive PCETs in subunit α involving α -Y₇₃₁, α -Y₇₃₀ and active site α -C₄₃₉. However, the mechanistic and kinetic details remain unsolved due to large conformational changes upon substrate and allosteric effector binding, masking spectroscopic detection of all intermediates [2].

We performed classical molecular dynamic simulations of the active $\alpha 2\beta 2$ complex, investigating the structural changes along the pathway. At the $\alpha 2\beta 2$ interface, β -Y₃₅₆ and α -Y₇₃₁ can be found in multiple conformations, indicating their role as "linker residues" for radical transfer across the interface [3]. We also performed QM/MM simulations with metadynamics to obtain the free energy profiles for the different PCET steps.

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A new tool for diabatization of electronic excitations

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A general method has been proposed^{1,2} for analyzing the electronic excitation character in terms of local Frenkel excitations (FE) and charge transfer excitations (CT), and for constructing the related quasi-diabatic states and coupling matrix elements. The method works for configuration interaction singles (CIS) wave functions, and can also (as an approximation) be applied to the second-order approximate coupled-cluster singles and doubles (CC2) and the second-order algebraic-diagrammatic construction [ADC(2)] methods. Recently full support of time dependent density functional theory (TDDFT) has been implemented as well and will be available in future releases of the TURBOMOLE program package. Some new applications on aggregated systems show that the for some hybrid functionals, i.e. B3LYP, and PBE0, the computed diabatic state coupling parameters are very similar to the ones of ADC(2) method, although TDDFT predicts the wrong order of the excited states.

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Calculation of NMR chemical shielding tensors with double-hybrid DFT. Development of DLPNO-MP2 second derivatives.

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Analytic calculation of nuclear magnetic resonance (NMR) chemical shielding tensors at the level of double-hybrid density functional theory (DHDFT) is implemented in the ORCA program, using gauge-including atomic orbitals and the resolution of the identity (RI) approximation for the second order Møller–Plesset perturbation theory (MP2) correlation contributions. A set of 15 small molecules is used to benchmark the accuracy of the results with respect to CCSD(T) (coupled cluster theory including single, double, and perturbative triple excitations) data, comparing also to calculations with MP2, Hartree–Fock, and commonly used pure and hybrid density functionals.

Chemical shifts obtained with the DSD-PBEP86 double-hybrid functional show the smallest mean absolute relative deviation from the reference data (1.9 %). This is a significant improvement over MP2 (4.1 %) and spin-component-scaled (SCS) MP2 (3.9 %), as well as the best-performing conventional density functional included in the study, M06L (5.4 %). A protocol for the efficient and accurate computation of chemical shifts at the DHDFT level is proposed after analysis of the errors due to basis sets, grid sizes, etc. Calculations with this approach are routinely applicable to systems of 100–400 electrons, being one to two orders of magnitude slower than equivalent calculations with conventional (pure or hybrid) density functionals. For larger systems a local correlation treatment is necessary for the MP2 contribution. First

steps towards NMR shielding calculations at the level of domain-based local pair natural orbital MP2 (DLPNO-MP2) are presented.



Figure 1: Relative deviations (%) of chemical shifts, calculated with different methods and the pcSseg-4 basis set, from CCSD(T)/pcSseg-4 values. Boxes denote interquartile ranges, whiskers denote minima and maxima, and diamonds denote means.

Quantum hydrodynamics approach for calculating non-zero current densities

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Quantum dynamics in molecules can be understood through the complete study of the probability and current densities, that is able to characterize the electron motion. The Born-Oppenheimer approximation (BOA) is one of the widely used approximation to calculate the probability densities. Unfortunately, the problem of vanishing electron current densities within the BOA occurs for vibrating or dissociating molecular systems in a single electronic state [1]. Some approaches and methods were introduced to overcome this problem, but we aim at the accurate calculation of current densities using the quantum hydrodynamics (QHD) approach. This approach is able to calculate non-zero current densities by solving numerically the Ehrenfest equation of motion [2]. In this poster, we use a simple model system of two interfering Gaussian wave packets moving in a harmonic potential to calculate the QHD current densities [3].

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Investigating the Effect of Missing Inter-Subsystem Charge-Transfer Excitations in Subsystem TDDFT

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For TDDFT-based calculations of response properties, e.g. excitation energies, of extended systems, fragmentation and embedding methods such as subsystem DFT and Frozen Density Embedding (FDE) [1–3] can be applied. Herein, three substantial approximations need to be considered: First, a restricted basis set is usually used compared to supermolecular calculations. Second, an approximate kinetic energy potential and kernel are employed. Third, charge-transfer (CT) excitations between subsystems are inherently omitted. While the first two error sources might have mild effects on local excitations, the third issue definitely creates a qualitative difference to supermolecular calculations.





Fig. 1: Comparison between TDDFT (blue) and subsystem TDDFT (FDEc, red) of the lowest excitations of an ethene \cdot ethyne complex.

Fig. 2: HOMO (left) and LUMO (right) of the TDDFT CT excitation at 120 nm.

FDE-TDDFT introduces another error, consisting in only intrasubsystem, i.e. local, excitations. Delocalized excitations as linear combination of various excitations on different subsystems can be obtained with Coupled FDE (FDEc) [2], which was developed especially for the description of excitonically coupled chromophores with a few prominent, intense low-energy excitations, but can also be used for more general problems. But even in FDEc, the issue concerning intermolecular charge-transfer excitations persists. In this work, we analyze the effects of such charge-transfer contributions by explicit comparisons of FDEc and supermolecular spectra over a broad spectral range.

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Influence of Dispersion Forces on Molecular Recognition in Solution

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Accurate description of non covalent interactions in solution is one major research interest of the scientific community, aiming for consistency to experiment or even predictive power. One experimental approach of measuring non covalent interactions is through specifically designed molecular balances. For these flexible systems the accurate representation of the molecular ensemble and consequently $T\Delta S$ is mandatory. In this work molecular balances in solution are investigated using a recently published, conformer/rotamer ensemble (CRE) generation algorithm[1] relying on the fast and robust semiempirical quantum chemical GFN2-xTB(GBSA) [2] electronic structure method. The CRE is then refined at the B97-3c[3] level of theory and free energies are calculated for each conformer employing an established multilevel ansatz. The calculated folding free energies are analyzed in comparison to experimental data[4].



Figure 1: Two folding states of a molecular balance in solution.

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The Impact of DNA-Confinement on The Photoisomerization of A Triazene: A PE-ADC(2) Study

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In a recent study [1], ADC(2) intrinsic reaction coordinate calculations on the DNA-minorgroove binder berenil disclose that the excited-state relaxation pathway to the S_1 minima/conical intersection comprises a two-step mechanism: N=N bond stretching followed by a bicyclepedal type rotation inside the triazene bridge. However, the effect of DNA-confinement, ground state dynamics and micro-environmental interactions on the relaxation mechanism of the DNAminor-groove binders are not yet fully understood.



To explore the role of the (bio-)molecular environment on the excited state relaxation pathways, we implemented the excitation energies and excited state molecular gradients of the ADC(2) within a QM/MM polarizable embedded scheme, PE-ADC(2) [2]. In this implementation of PE-ADC(2), the polarization-correlation cross terms for the ground and excited states are included via an approximate coupling density. Moreover, the Pauli repulsion of an MM site is estimated via an effective core potential (ECP) to avoid the so-called charge leaking problem. The initial findings about the effect of DNA-confinement on the photoisomerization mechanism will be discussed in the poster presentation.

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The role of dispersion in the structure of diphenyl ether aggregates

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Dispersion interactions can play an important role to understand unusual binding behaviors. This is illustrated here by a systematic study on the structural preferences of diphenyl ether (DPE)-alcohol clusters, for which either an OH-O or an OH- π -bound isomer can be found. The alcohol molecules range from methanol to adamantanol. Investigations of the DPE-water complex complete this series. The experimental investigations are performed by IR/UV methods, microwave spectroscopy, and FTIR spectroscopy, tightly connected with a detailed theoretical analysis presented in this contribution[1]. The resulting solvent-size-dependent trend on the structural preference turns out to be counter-intuitive, i.e., the hydrogen-bonded OH-O structures become more stable for larger alcohols, which are expected to be stronger dispersion energy donors and thus should prefer an OH- π arrangement. Quantification of dispersion interactions *via* LMP2 calculations yielding dispersion interaction densities[2] and the consideration of the twisting of the ether upon solvent aggregation are found to play a key role for understanding this preference.



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Theoretical investigation of the solubilities of AgI and AgTcO₄

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In order to depict the thyroid radioactive isotopes are used in radiology. The two specific hormones of the thyroid (tyroxine and triiodothyronine) both contain considerable amounts of iodine. Thus the radioactive iostope ¹²³I is enriched in the thyroid gland. The pertechnetate anion TcO_4^- is of the same size as the iodide anion I⁻ and is therefore also enriched in the tyroid. Both metastable technetium ^{99m}Tc and ¹²³I are γ emitters, but ^{99m}Tc has both a lower half-live and a considerably lower γ energy. Thus, ^{99m}TcO_4^- is preferred to ¹²³I⁻ in radio diagnostics.

Even though both the iodide anion and pertechnetate anion have the same size in aqueous solution, I⁻ is a soft base whereas TcO_4^- is a hard base according to Pearson's HSAB concept. This should be noticeable in the solubility of their salts with the soft acid Ag⁺. Indeed, the solubility product of AgTcO₄ is $4.4 \cdot 10^{-4}$, whereas it is only $8.5 \cdot 10^{-17}$ for AgI.

It is the aim of this work to investigate the difference in solubility of these two compounds. The solid state is described using the periodic DFT-Code VASP[2]. For the solution, also experimental data have to be taken into account, e. g. [3].

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Polarizable Embedding Combined with the Algebraic Diagrammatic Construction: Investigating Electronic Excitations in Biomolecular Systems

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We present a novel variant of the algebraic diagrammatic construction (ADC) scheme by combining ADC with the polarizable embedding (PE) model[1]. The PE-ADC method is implemented through second and third order and is designed with the aim of performing accurate calculations of excited states in large biomolecular systems. Contributions of the polarizable environment are taken into account through a self-consistent PE-HF ground state and *a posteriori* state-specific and linear-reponse-type corrections of the excitation energies. Easily accessible transition and difference densities make computation of such corrections particularly easy and efficient in our ADC framework[2] in the Q-Chem program package [3]. Using this densitydriven approach, PE-ADC in principle works for any method of the ADC family. We demonstrate how our combined method can be readily applied to study photo-induced biochemical processes as we model the charge-transfer (CT) excitation which is key to the photoprotection mechanism in the dodecin protein. State-of-the-art excited state analysis shows the role of the polarizable environment in stabilizing the pivotal CT state in dodecin.

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An Efficient Lossless Compression Algorithm for Trajectories of Atom Positions and Volumetric Data

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Simulation trajectories are often large files and put high demands on disk storage systems. This is even more the case if volumetric data on a grid (e. g., electron density) shall be stored along the trajectory. Such volumetric data trajectories possess many useful applications, including the prediction of bulk phase VCD and ROA spectra from electron density, as we have recently shown.^{3,4} On this poster, we present our newly developed and highly efficient lossless compression algorithm for trajectories of atom positions and volumetric data.^{1,2} The algorithm is designed as a two-step approach. In a first step, efficient polynomial extrapolation schemes reduce the information entropy of the data by exploiting both spatial and temporal continuity. The second step processes the data by a series of transformations (Burrows-Wheeler, move-to-front, run length encoding), and finally compresses the stream with multi-table canonical Huffman encoding. Our approach reaches a compression ratio of around 15:1 for typical position trajectories in XYZ format. For volumetric data trajectories in Gaussian Cube format (such as electron density), even a compression ratio of around 35:1 is yielded, which is by far the smallest size of all formats compared here. At the same time, compression and decompression are still reasonably fast for everyday use. The precision of the data can be selected by the user. For storage of the compressed data, we introduce the

BQB file format, which is very robust, flexible, and efficient. In contrast to most archiving formats, it allows fast random access to individual trajectory frames. Our method is implemented in C++ and provided as free software under the GNU LGPL license. It has been included in our TRAVIS program package,⁵ but is also available as stand-alone tool and as a library ("libbqb") for use in other projects.¹



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Variational ro-vibrational calculations for linear tetra atomic molecules using Watsons isomorphic Hamiltonian

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Variational ro-vibrational calculations for small molecules with up to 3 atoms are nowadays a routine task [1,2]. By employing an accurate potential energy function it is possible to achieve so called "spectroscopic accuracy" of 1 cm⁻¹ for a large variety of small linear molecules [3-5]. However, ro-vibrational calculations for linear molecules with more than 3 atoms are still rather scarce [6-9]. A new variational program will be presented that is able to calculate ro-vibrational term energies and wave functions of linear tetra atomic molecules. The calculations are based on Watsons isomorphic Hamiltonian for linear molecules [10] and the ro-vibrational wavefunctions are expanded in a basis of one and two dimensional harmonic oscillators for the stretching and the bending vibrations, respectively, as well as rigid-rotor functions for the rotation. Special attention will be given to the coordinate transformation from normal to internal coordinates. An efficient nested hybrid MPI/OMP parallelization enables the calculation of converged energy levels. Finally, comparisons to known results obtained variationally are presented.

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Self-assembled monolayers (SAMs) of thiol-containing organic molecules grafting on gold surface: a first-principles study

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The performance of organic field effect transistors (OFETs)^[1] is highly influenced by the properties of the electrode/semiconductor interface. The interface generally has an energy barrier which prevents the charge carriers from passing the interface. Interfacial engineering^[2] by covalently binding self-assembled monolayers (SAMs)^[3] of dipolar organic molecules on the electrode surface can further modify the relative energy level positions on either side of the interface^[4], thereby minimizing the charge-injection barrier.

Based on first-principles calculations, we study the equilibrium geometries, electronic and optoelectronic properties of SAMs of thiol-containing organic molecules grafting on the Au (111) surface, as shown in Fig. 1 (b). The binding modes, tilt angles of the low-energy adsorption configurations, and their corresponding band structures, partial density of states, work functions, and IR spectra are investigated. The calculated results are compared with experimental results.



Fig. 1: (a) Scheme of a dipolar molecule modifying the electrode/semiconductor interface. The symbol μ indicates the dipole moment of the molecule, and α is tilt angle of the molecule relative to the electrode surface. (b) The SAM of the dipolar molecule grafting on Au (111) surface.

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Exchange-hole-normalization-DFT (xhn-DFT): A simple model for multi-reference systems

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Strongly correlated (multi-reference) electronic ground states represent a major challenge within density functional theory (DFT). The description of such electronic structures within a single Kohn-Sham determinant [1] requires an ensemble-state representation using fractionally occupied orbitals [2, 3]. The use of fractional occupation numbers, however, lead to non-normalized exact-exchange holes, which is not considered by conventional approximative density functionals, resulting in large fractional-spin errors.

Inspired by Johnson's strong correlation functional [4], we developed a simple approach to incorporate the exact-exchange-hole normalization into DFT at only marginally higher computational cost. This new method, denoted as exchange-hole-normalization DFT (xhn-DFT) [5], is generally applicable to any pure functional up to the meta-GGA level. Compared to conventional DFT, the xhn-DFT model strongly improves the description of multi-reference systems, while preserving the accuracy of DFT in the single-reference case. The accuracy of the new method is analyzed for spin-averaged atoms and spin-restricted bond dissociation energy surfaces, exemplifying typical multi-reference problems.

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Hybrid particle-field molecular dynamics simulations of a charged surfactant

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Surfactants find use as detergents in many areas of daily life such as, e.g., in tooth pastes or shampoos. This class of molecular compounds is able to aggregate into numerous different macro structures such as micelles or bilayers.[1] In our hybrid particle-field simulations of the amphiphile sodium dodecyl sulfate (SDS) in aqueous solution we observed the formation of spherical and worm-like aggregates depending on the concentration of additional sodium chloride (NaCl) in solution. We studied the morphology of the aggregates as a function of SDS and NaCl concentration and found the behavior represented in Fig 1.



Figure 1: Concentration of SDS and NaCl used in the simulations. Red dots represent spherical micelles and blue dots elongated tubes. The gray area indicates a transition area where both morphologies occur.

Our results qualitatively agree with those from scattering experiments.[2] We were able to find the driving forces for and the mechanism of the transformation and explain our findings with a simple model for the free energy of the system.

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Influence of vibrational excitations on the photoisomerization of bacteriorhodopsin with OM3-MRCI/Amber

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Bacteriorhodopsin (bR) is a photo-driven proton pump in archaea bacteria like halobacterium salinarium. These organisms use bR to produce ATP. Proton pumping is triggered by photoisomerization of all-trans retinal, which is covalently bound through a Schiff base linkage to one of the protein helices. Within a half picosecond, the 13-cis form is generated with a quantum yield of 0.65. This step induces a series of thermal reactions that finally transport a proton from the intracellular region to the outside of the cell. The efficiency of the isomerization highly depends on the nature of the surrounding protein residues and on the hydrogen bonded network next to the protonated Schiff base, this has been shown in numerous mutation studies. [1] A key mode in Schiff base photoreactions is the hydrogen outof-plane vibration at the isomerizing double bond. This motion controls the outcome of the photoreaction. [2] When the hydrogen motion and the reaction coordinate are in-phase at the S_1/S_0 crossing, the product will be mainly 13-cis. In this study, we use the semiempirical OM3-MRCI method developed by Thiel et al. [3] to investigate the influence of external vibrational excitations on the lifetime and the product ratio of the photodynamics, exciting the C13=C14 hydrogen-out-of-plane, C13=C14 torsion or C=C in-plane modes in the electronic ground state. QM/MM surface hopping molecular dynamics [4] with decoherence correction are performed with a new version of the COBRAMM QM/MM suite developed in Bologna, Lyon and Düsseldorf. [5] The computations reveal a significant impact on the photoreaction, when the key modes are excited by three to six additional quanta. We compare different levels of QM/MM partitioning and crystal structure models differing in the configuration of retinal structure and orientation of nearby residues.

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Influence of bridge proton position on the interaction energy of homodimers of molecules with intramolecular hydrogen bonds

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Our recent investigations of correlation between proton motions in two intramolecular hydrogen bridges of "zwitterionic proton sponge", 1,8-bis(dimethylamino)-4,5-dihydroxy-naphthalene, [1] have indicated rather moderate preference for the "trans" arrangement. That study, based on the Car-Parrinello molecular dynamics (CPMD) [2], revealed also very small influence of environment (gas phase vs. molecular crystal) and dispersion corrections. However, in many other cases the impact of the neighboring molecules is very strong and the proton position in the intramolecular hydrogen bridge differs strongly between the gas phase and solid state conditions. The current report shows how the change of the proton position in the bridge of one of the molecules changes the interaction strength between this molecule and its immediate neighbor. A simple reasoning to explain such change is based on the change of the molecular dipole moment when the bridge proton is displaced. Thus, the simple electrostatic dipole-dipole interaction is altered.

The homodimers of selected molecules with intramolecular hydrogen bonds were prepared on the basis of their crystal structures, i.e. cut out of the crystal so that the stacking arrangement of the molecules was obtained. The distance between the molecular planes was kept frozen, but the rest of the structural parameters were allowed to be optimized during the scanning of the proton positions. The DFT approach with D3 dispersion corrections of Grimme was used, and the molecular orbitals were described with the help of the def2-TZVP basis set. The set of chosen molecules includes the aforementioned "zwitterionic proton sponge" [1], quinoline *N*-oxide derivatives [3] and *o*-hydroxy Schiff base derivatives. These compounds were previously investigated by us using the CPMD approach and diverse cases of environmental impact on the intramolecular hydrogen bridge were registered.

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A practical approach to intramolecular interactions via molecular fragmentation

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We present an efficient molecular fragmentation method for the accurate description of intramolecular interactions [1]. In this method, a molecule is represented by a sum of distinct bonded and non-bonded fragments. In order to reduce errors in the approach which stems e.g., from the missing intramolecular polarization interactions, an incremental correction scheme is applied by performing the fragmentation at various levels with varying fragment sizes. The non-bonded contributions are accounted for on an *ab initio* electron correlation level in our approach using either the supermolecular or intermolecular perturbation theory method. The latter approach allows to further decompose the intramolecular interaction energy into physically interpretable interactions. The application of the fragmentation method on sterically crowded hydrocarbons demonstrates the intricate balance of attractive and repulsive contributions of the intramolecular interaction that governs the stability of the molecules [2, 3].

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Wave Packet Dynamics of Indistinguishable Particles with Contracted Orbitals

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Time dependent quantum dynamics of systems containing indistinguishable particles is an important topic in chemistry and condensed matter physics. Last year the multi layer multi configuration time dependent Hartree method in optimized second quantisation (ML-MCTDH-oSQR), combining the advantages of two former theories, was published[1]. It uses the tensor contraction scheme of the multi layer multi configuration time dependent Hartree method in second quantisation developed by Wang and Thoss[2] as well as optimized orbitals like the multi configuration time dependent Hartree method for fermions[3] and bosons[4]. With the ML-MCTDH-oSQR method the time evolution of quantum states for indistinguishable particles can be described. On the one hand a time dependent orbital basis is adapted to the dynamics of the evolution of the quantum states. On the other hand the time dependent quantum states are represented in configuration space build up out of this optimized orbitals. A tensor contraction is used to reduce the size of the configuration space. Note that both orbitals and states are optimized simultaneously. It was already shown that the ML-MCTDH-oSQR method is an efficient way to describe real time quantum dynamics of systems with non constant particle number. Now this method is extended by an additional tensor contraction in the space of orbitals, such that one can use bigger orbital basis sets. This improves the speed of calculations if one has more than one spacial dimension as it is usually the case in chemistry. We will present some theoretical insides and an small numerical example.

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Finding a Starting Guess for Transition Structure Optimisations: A Parallelised Auto-Adjusting Reaction Path Optimiser

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In order to get a sufficiently accurate guess for a transition structure (TS) the woelfling program [1] as implemented in TURBOMOLE was modified. The woelfing program optimises a reaction path (RP) between two intermediate structures to approximate the minimum energy path (MEP) with a finite number of images. In contrast to the conventional nudged elastic band (NEB) approach [2] there are no spring forces involved to enforce equal spacing between the images. Instead a predefined distribution of the images in the cartesian space is directly used as a constraint in the optimisation algorithm. A frequent problem of such algorithms can occur when the RP contains a lot of structural rearrangement and therefore no image ends up being sufficiently close to the desired TS. By simply utilising more images a better guess for the TS can be obtained, hence the woelfling program was parallelised. This was an embarassingly easily parrellelisation problem, since the images can be calculated separately. Another approach is to pick images in the region close to the intermediates as new start or end points as soon as they become sufficiently converged with respect to the previous optimisation step. The approach seems practical since the convergence in this region is much faster than close to the TS. Thereby one obtains a shortened section of the RP, naturally increasing the likelihood of the images ending up close to the TS. This is somewhat similar to the climbing image NEB method by Henkelman et al. [3], but instead of one image the path-limiting images climb up the RP.



Figure 1: Exemplary RP optimisation and climbing step of a ring opening reaction.

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Embedding QM:QM Methods for Molecular Crystals

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In recent years, advances in method developments have been leading to increasingly accurate predictions of structures of molecular crystals. This has been highlighted by the impressive results in the prediction of crystal structures for organic molecules and, recently, also organic salts.[1] Much of this progress can be attributed to the increased application of density functional theory (DFT) including dispersion corrections (+D) using periodic boundary conditions.

An alternative to such periodic DFT+D approaches within quantum mechanical methods is to embed one quantum mechanical in another quantum mechanical model within a many-body QM:QM scheme.[2-4] Here, we present calculations for the X23 benchmark set of molecular crystals[3], for which various DFT+D and semi-empirical approaches as well as QM:QM methods are tested. For the latter, we introduce a combination of PBE0:PBE+D3, PBE0:PBE+MBD, B3LYP:BLYP+D3[3], and BLYP:DFTB3+D3[4], yielding results which are extremely close to either the parent hybrid or the GGA functionals.

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Allosteric control of pH-sensitive Ca(II)-binding in langerin

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The dendritic C-typ lectin receptor langerin plays an important part for the inert human immune response. Due to a high specificity for mannose, it binds invading pathogens like HIV and releases them after endocytosis for degradation (Fig. 1).[1] The protein relies on a calcium(II)-cofactor, while its calcium-binding affinity is pH-dependent. The sidechain of a histidine (H294) was already identified as partial pH-sensor which is particularly interesting, because this residue has no direct contact to the calcium-binding site (Fig. 1).[2] The effect of the additional proton therefore needs to be transported by some kind of allosteric mechanism.



Langerhans-Zelle

Figure 1 Schematic illustration of langerins function as dendritic receptor.

Figure 2 Structure of the langerin carbohydrate recognition domain.

Several microseconds of classical, atomistic molecular dynamics simulations of the holo- and the apo-protein in different protonation states are currently analysed and compared. The data is used for the construction of kinetic Markov state models to capture the conformational dynamics of the systems and to identify metastable functional states.

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Combining Effective Fragment Potentials with ADC: theory and benchmarks

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Modelling environment effects on embedded chemical systems is important for understanding the underlying chemistry in many photochemical and photo-physical processes. There are many approaches to include solvent-solute interactions through both implicit and explicit solvent models. The EFP (Effective Fragment Potential) method, based on parameters derived from *ab intio* calculations is one promising approach for modelling the solvent effects on the embedded system [1]. In addition, ADC methods for the polarization propagator have already been established for studying excited states and their properties [2]. They are widely applied to a broad spectrum of molecular systems exploiting already existing solvent models.

Present work focusses upon investigating the accuracy of EFP-ADC in simulating singlet and triplet excitation energies along with oscillator strengths for a set of molecules. Therefore, a benchmark has been carried out over test systems with a varied level of interaction strength keeping super-molecular ADC(n) as a reference against EFP-ADC(n) calculations. A total of 80 singlet and triplet states are considered for the benchmark of EFP-ADC(2), and 55 singlet and triplet states are included for examining the accuracy of EFP-ADC(3). Overall, a mean signed error of -0.021 eV with a standard deviation of 0.049 eV has so far been observed for systems with one water molecule as solvent. The study is being extended to systems different solute-solvent interaction strengths and to with solvents with varied polarities such as acetonitrile, chloroform and methanol.

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Exploring Proton Conduction Properties in Pure 1,2,3-Triazole Phases via AIMD

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Over the last decades triazoles rised to a hot topic in science. This is mainly due to the use within the concept of click chemistry[1, 2] and their proton conducting properties[3]. For the second unfortunately not much is known on a molecular scale. Therefore we set up 4 AIMD simulations of pure triazoles at four temperatures (liquid and solid phases) for an insight into the Ångström scale. As the results of this study not only the experimental data for the mobility of protons in pure triazoles were reproduced[4] even a suggestion of a possible mechanism in solid phase was made. Structure (see Fig.1) and dynamics of the simulated systems give raise to extract properties for mixed or triazole embedded systems[3] to tune those as desired.



Figure 1: A selected part of the orthorhombic system (280 K). On the left side the front view of the proton conducting wire and on the right side the wire from above is shown. In red and blue nitrogen atoms of the corresponding tautomer are shown.



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