18TH CENTRAL EUROPEAN SYMPOSIUM ON THEORETICAL CHEMISTRY 2022

7th - 10th September, 2022
Balatonszárszó, Hungary

PROGRAM AND BOOK OF ABSTRACTS

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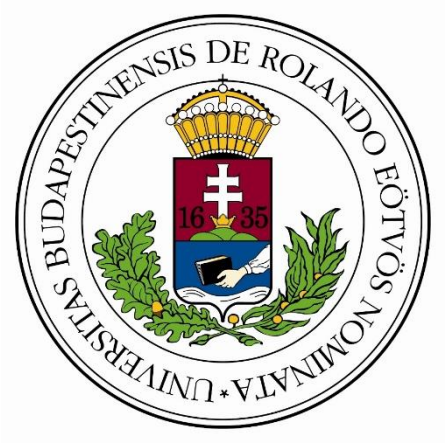
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18th Central European Symposium on Theoretical Chemistry 2022

Lecturis salutem!

The local organizers of the 18th Central European Symposium on Theoretical Chemistry (CESTC) most gladly welcome the CESTC community in Hungary, at the southern cost of lake Balaton, following an unexpected and least desired three years pausa of the series. We sincerely hope for this series of Symposia getting back to its traditional yearly schedule, from now.

Getting together year by year, we could meet most of our old friends, share currents news and enjoy each others company. We also had the opportunity of getting acquainted with a new generation of young quantum chemists, entered our discipline in the past year. This timespan now being increased to three years, we expect to see many faces new to the series and especially welcome them! We do hope that they will be eager to follow the CESTC traditions.

The CESTC in 2022 is special in one more respect, since this is the first year to greet our Croatian colleagues as part of the Scientific Board. They formerly attended CESTC as guests and joined to the official Organizing Committee on this occasion.

While CESTC is a regional event in the first place, participation of a few colleagues from non-CESTC countries is traditionally endorsed. This year we solicited lecturers from Romania and India and have the pleasure of welcoming them together with attendees from some more countries beyond Central-Europe.

We wish all of you a fruitful meeting, and hope for splendid weather allowing you to enjoy the early-autumn Balaton.

Yours, cordially

Péter Surján Ágnes Szabados Péter G. Szalay

18th Central European Symposium on Theoretical Chemistry 2022
7th - 10th September, 2022
SDG Family Hotel & Conference Center

Programme

September 7th (Wednesday)

9:00 - Arrival and registration

13:20 - 13:30 Opening

Chair: Péter G. Szalay

Invited Lectures

13:30 - 14:00 **Olga Malkina** - *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia*
A mystery of a through-space indirect NMR spin-spin coupling between two hydrogen atoms

14:00 - 14:30 **Zdenek Futera, Outi Vilhelmiina Kontkanen, Denys Biriukov** - *Faculty of Science, University of South Bohemia, Czech Republic*
Electron transport on biomolecular interfaces with metal electrodes

Oral Lecture

14:30 - 14:50 **Michał Lesiuk** - *Faculty of Chemistry, University of Warsaw, Poland*
High-level coupled-cluster methods with tensor decomposition

14:50 - 15:10 Coffee break

Chair: Jozef Noga

Invited Lecture

15:10 - 15:40 **Radu Silaghi-Dumitrescu** - *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania*
Spectral simulations for bioinorganic centers: in the eye of the beholder

Oral Lectures

15:40 - 16:00 **Matej Uhliar; Denisa Mastiľák Cagardová; Ján Matúška** - *Department of Chemical Physics, Slovak University of Technology in Bratislava, Slovakia*
On aromaticity and electronic properties of selected organic molecules: a theoretical study of relation between the two

16:00 - 16:20 **Michael Bakker; Jana Pavlikova; Amina Gaffour** - *Charles University, Hradec Kralove, Czech Republic*
Probing disordered proteins' phase space of NMR chemical shifts with fragmentation and machine learning

16:20 - 16:40 **Katarzyna Jakubowska; Magdalena Pecul; Kenneth Ruud** - *Faculty of Chemistry, University of Warsaw, Poland*
Vibrational corrections to NMR spin-spin coupling constants from relativistic four-component DFT calculations

16:40 - 17:00 Coffee break

Chair: Nađa Došlić

Invited Lecture

17:00 - 17:30 **Bence Balázs Mészáros; János Daru** - *ELTE Eötvös Loránd University, Hungary*
Pushing mechanistic studies to the limits. But in which direction?

Oral Lectures

17:30 - 17:50 **Péter Pál Fehér, Ádám Madarász, András Stirling** - *Research Centre for Natural Sciences, Hungary*
Benchmarking computational approaches for the prediction of molecular properties pivotal in photocatalysis

17:50 - 18:10 **Dóra Vörös, Andrea Angeletti, Cesare Franchini, Sebastian Mai, Leticia González** - *Institute for Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Austria*
Adsorption and photochemistry of a functionalized push-pull stilbene

18:10 - 18:30 **Mihael Eraković; Marko T. Cvitaš** - *Ruđer Bošković Institute, Croatia*
Instanton approach for simulation of vibration-rotation-tunneling spectra of multi-well systems

18:30 - 19:30 Supper

19:30 - Poster section I.

September 8th (Thursday)

Chair: Jiří Pittner

Invited Lecture

09:00 - 09:30 **Robert W. Góra** - *Faculty of Chemistry, Wroclaw University of Science and Technology, Poland*
Photochemical origins of life elucidated by *ab initio* quantum chemistry

Oral Lectures

09:30 - 09:50 **Tomislav Piteša, Marin Sapunar, Nađa Došlić** - *Ruđer Bošković Institute, Croatia*
Diabatization of electronic states along nonadiabatic trajectories

09:50 - 10:10 **Michał Hapka; Michał Przybytek; Katarzyna Pernal** - *Faculty of Chemistry, University of Warsaw, Poland*
Symmetry-adapted perturbation theory based on multiconfigurational wave function description of monomers

10:10 - 10:50 Coffee break

Chair: Miroslav Medved

Invited Lecture

10:50 - 11:20 **Lukas Bucinsky** - *Slovak University of Technology, Bratislava, Slovakia*
Quantum crystallography. An overview, and issues related to the presence of heavy elements.

Oral Lectures

11:20 - 11:40 **Péter Jeszenszki; Dávid Ferenc; Edit Mátyus** - *ELTE Eötvös Loránd University, Hungary*
Variational Dirac–Coulomb approach with explicitly correlated basis functions

11:40 - 12:00 **Michał Przybytek** - *Faculty of Chemistry, University of Warsaw, Poland*
He_3 interaction potential: asymptotic behavior of the post-Born-Oppenheimer corrections

12:00 - 13:30 Lunch

13:30 - 18:30 Free

18:30 - 19:30 Supper

19:30 - Poster section II.

September 9th (Friday)

Chair: Géza Fogarasi

Invited Lecture

09:00 - 09:30 **Antonio Prlj; Basile F. E. Curchod** - *University of Bristol, United Kingdom*
Investigating sunlight-triggered excited-state dynamics of transient atmospheric molecules

Oral Lectures

09:30 - 09:50 **Michal Belina; Petr Slavíček; Kirsten Andrea Schnorr** - *University of Chemistry and Technology, Department of Physical Chemistry, Czech Republic*
Direct observation of the fastest acid-based reactions: combining FEL experiments with *ab initio* theory

09:50 - 10:10 **Anna Grabarz; Borys Ośmiałowski** - *Faculty of Chemistry, Wroclaw University of Science and Technology, Poland*
Application of modern density functionals in modeling of excited states of organic dyes

10:10 - 10:50 Coffee break

Chair: A. Daniel Boese

Invited Lecture

10:50 - 11:20 **Sourav Pal** - *Indian Institute of Science Education and Research Kolkata; Visiting Professor, Ashoka University, Sonipat, Haryana, India*
Complex absorbing potential based coupled cluster method for resonance and decay

Oral Lectures

11:20 - 11:40 **Gabriel Rath, Wassja A. Kopp, Kai Leonhard** - *Institute of Technical Thermodynamics, RWTH Aachen University, Germany*
Accurate anharmonic partition functions using low-cost Hamiltonians and Monte Carlo Integration

11:40 - 12:00 **Julianna Oláh; Zsolt Benedek; Marcell Papp; Joseph Kfoury; Tibor Szilvási** - *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Hungary*
The mechanism of biomimetic nitrogen fixation: insights from quantum chemistry and microkinetic modelling

12:00 - 13:30 Lunch

Chair: Pavel Neogrády

Invited Lectures

13:30 - 14:00 **Joanna Jankowska** - *Faculty of Chemistry, University of Warsaw, Poland*
To infinity, and beyond: expanding the *on-the-fly* NAMD capabilities for modeling cutting-edge photophysical phenomena

14:00 - 14:30 **Alexandru Lupan, Amr A. Attia, Szabolcs Jákó, Attila-Zsolt Kun, R. Bruce King** - *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Romania*
Unusual non-spherical deltahedra in metallaborane structures

Oral Lecture

14:30 - 14:50 **Jakub Lang; Michal Przybytek; Michal Lesiuk; Bogumil Jeziorski** - *Faculty of Chemistry, University of Warsaw, Poland*
Ab initio study of three-body polarizability of helium

14:50 - 15:10 Coffee break

Chair: Robert W. Góra

Invited Lecture

15:10 - 15:40 **Tomica Hrenar** - *Department of Chemistry, University of Zagreb Faculty of Science, Croatia*
Building potential energy surfaces *on-the-fly* by deep learning

Oral Lectures

15:40 - 16:00 **Piotr Wróbel; Piotr Kubisiak; Andrzej Eilmes** - *Faculty of Chemistry, Jagiellonian University in Cracow*
AIMD simulations in modelling IR spectra of liquids

16:00 - 16:20 **D. Mišenková; F. Lemken; M. Repiský; J. Noga; O. L. Malkina; S. Komorovský** - *Institute of Inorg. Chem., Slovak Academy of Sciences, Slovakia*
Overcoming the gauge problem for g-tensor calculations in the framework of four-component DFT

16:20 - 16:40 **Milan Ončák; Magdalena Salzburger; Gabriel Schöpfer; Christian van der Linde; Ethan Cunningham; Martin K. Beyer** - *Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria*
Master Equation Modeling of Black Body Infrared Radiative Dissociation

16:40 - 17:00 Coffee break

Chair: Péter Surján

Invited Lecture

17:00 - 17:30 **Paul G. Mezey** - *Kyoto University, Japan; Eötvös Loránd University, Hungary*
Bonding Between Molecular Fragments Shows the Flaws of Persistent Pre-Quantum Chemistry Models

Oral Lectures

17:30 - 17:50 **Dennis F. Dinu; Martin Tschöpe; Benjamin Schröder; Klaus R. Liedl; Guntram Rauhut** - *Deparment of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria; Institute for Theoretical Chemistry, University of Stuttgart, Germany*
Spectroscopic constants from rovibrational configuration interaction calculations

17:50 - 18:10 **Michal Malček; Lukáš Bučinský** - *Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Slovakia*
Modified graphene quantum dots as hydrogen storage devices

18:10 - 18:30 **Valera Veryazov** - *Theoretical Chemicstry, Lund University, Sweden*
How to apply multiconfigurational theory to ionic solids?

18:30 - 18:50 **József Csóka** - *Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Hungary*
Analytic gradients for local density fitting Hartree-Fock and Kohn-Sham methods

19:00 - Conference dinner

September 10th (Saturday)

Chair: Tomica Hrenar

Invited Lecture

09:00 - 09:30 **Ctirad Červinka; Petr Touš** - *Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czechia*
Anisotropy, local disorder and polymorphism of molecular crystals

Oral Lectures

09:30 - 09:50 **Kamil Tokár; Matej Uhliar; Mariana Derzsi** - *Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava; Institute of Physics, Slovak Academy of Sciences, Slovakia*
The first silver chloride with rare silver clusters from *ab initio* study

09:50 - 10:10 **Michal Novotný; František Karlický** - *Department of Physics, Faculty of Science, University of Ostrava, Czech Republic*
Chemistry of Mxene terminal groups and their effect on layer cohesion

10:10 - 10:30 Coffee break

Chair:

Invited Lecture

10:30 - 11:00 **Maren Podewitz** - *Institute of Materials Chemistry, TU Wien, Vienna, Austria*
Predicting Reactivity and Selectivity of Transition-Metal Catalysts - Improving Accuracy Beyond Electronic Structure Theory

Oral Lectures

11:00 - 11:20 **M. Biela, E. Klein** - *Department of Chemical Physics, Slovak University of Technology in Bratislava, Slovakia*
Mechanisms of antioxidant action of phenolic acids and their carboxylate anions

11:20 - 11:40 **Johannes Hoja; A. Daniel Boese** - *University of Graz, Austria*
Benchmarking anharmonic vibrational frequencies of molecular dimers

11:40 - 12:00 **Vladimir Malkin, Florian Lemken, Stanislav Komorovsky, Olga Malkin** - *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia*
Visualization of EPR Hyperfine Structure Coupling Pathways

12:00 - 12:05 Closing

12:05 - Lunch

Poster section

7th September (Wednesday) P1 - P19
8th September (Thursday) P20 - P38

P1 **Ahmed Shaalan Alag; Dávid P. Jelenfi, Attila Tajti; Péter G. Szalay** - *György Hevesy Doctoral School, ELTE Eötvös Loránd University, Hungary*
Accurate evaluation of coupled cluster ionization potentials and electron affinities via excitation energy calculations

P2 **Nissrin Alharzali, Hisham Khalifeh Al Rawas, Sonia Taamalli, Abderrahman El Bakali, Florent Louis, Ivan Černušák, Duy Quang Dao** - *Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Slovakia*
A theoretical study of the OH-initiated atmospheric degradation of pentachlorophenol.

P3 **Andrej Hurajt, Martin Znava, Beatrice Karg, Mina Maddah, Magdalena Kowalska, Andrej Antusek** - *ATRI, Slovak University of Technology, Bratislava, Slovakia*
NMR shielding calculations of beta-NMR probe nuclei in ionic liquids.

P4 **Bónis Barcza; Ádám B. Szirmai; Attila Tajti; Péter G. Szalay** - *ELTE Eötvös Loránd University, Institute of Chemistry, Hungary*
Comparison of different model potentials for non-covalent interactions between N-heterocycles in ground and excited state

P5 **Johannes Hoja; Alexander List; A. Daniel Boese** - *Institute of Chemistry, University of Graz, Austria*
Development and Assessment of QM:QM Methods for Molecular Crystals

P6 **Martin Breza** - *Faculty of Chemical and Food Technology STU, Bratislava, Slovakia*
DFT studies of dimethyl amino phenyl substituted silver phthalocyanine

P7 **Šimon Budzák; Jakub Joniak; Henrieta Stankovičová; Milan Sýkora; Katarína Gaplovská-Kyselá; Marek Cigáň** - *Department of Chemistry, Matej Bel University, Banská Bystrica, Slovakia*
Rigidized 3-aminocoumarin fluorescent pH probes for acidic conditions

P8 **S. Forndran, N. Bersenkowitsch, C. van der Linde, M. Ončák, M. K. Beyer** - *Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität, Innsbruck, Austria*
Photodissociation of sodium iodide clusters doped with 5-bromovalerate

P9 **Michael Hütter; Ethan Cunningham; Christian van der Linde; Martin K. Beyer; Milan Ončák** - *Institute for Ion- and Applied Physics, University of Innsbruck, Austria*
Photoinduced charge-transfer processes in cesium iodide cluster ions

P10 **Dominik Jank; Miriam Meyer; Arne Schiller; Paul Scheier; Andrew Ellis; Milan Ončák** - *Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria*
Vibrational and Electronic Spectroscopy of $(C_{60})_n^{\pm}$-Clusters.

P11 **Erik Kalla, Hugo Semrád, Miriama Mateášová and Markéta Munzarová** - *Department of Chemistry, Masaryk University*
DFT Analysis of Diels-Alder Reactions for the preparation of forskolin derivatives

P12 **Joseph Kfoury; Frank Blockhuys; Julianna Oláh** - *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Hungary*
Understanding the Effect of the Transition Metal on the Properties of Cyclopentadienyl-stabilized 5,1,3,2,4-Metalladithiadiazoles

P13 **Ahmed M. Rozza; Mary Jo Ondrechen; Julianna Oláh** - *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economic, Hungary*
Effect of dual phosphoprylation on the activation mechanism of ERK2: computational insights

P14 **Andrea Kováčová** - *Department of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Slovak Republic*
On quantum chemical calculations of acidity constant of phenol derivatives and their cation radical forms

P15 **Ádám Margócsy; Ágnes Szabados** - *ELTE Eötvös Loránd University, Faculty of Science, Institute of Chemistry, Hungary*
A novel treatment of redundancy in Multi-Configuration Perturbation Theory

P16 **Ján Matúška; Lukáš Bučinský, Marek Štekláč, Marián Gáll; Michal Pitoňák** - *Institute of Physical Chemistry and Chemical Physics FCFT SUT, Bratislava, Slovakia*
Prediction of docking scores to the main protease M^{pro} by machine learning

P17 **Adèle D. Laurent, Habiburrahman Zulfikri, Claudia Filippi, Miroslav Medveď** - *Department of Chemistry, Faculty of Natural Sciences, Matej bel University, Slovakia; RCPTM CATRIN, Palacky University Olomouc, Czech Republic*
Computational insights into photochromic behavior of iminothioindoxyls

P18 **Martyna A. Osada; Michał Tomza** - *University of Warsaw, Poland*
Accurate *ab initio* calculations for the alkali-metal and alkaline-earth-metal hydrides

P19 **Tomáš Ovad; Marin Sapunar; Štěpán Sršeň; Petr Slavíček; Zdeněk Mašín; Juraj Fedor** - *University of Chemistry and Technology, Prague, Czech Republic*
Excitation and fragmentation of SF_6-replacement dielectric gas C_3F_7CN: electrons vs. photons

P20 **Kemal Önen; Dennis F. Dinu; Klaus R. Liedl** - *Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria*
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Multireference and relativistic DMRG-tailored CC methods.

P22 **Marin Sapunar; Petr Slavíček; Zdeněk Mašín** - *Department of Physical Chemistry, University of Chemistry and Technology; Institute of Theoretical Physics, Charles University, Prague, Czech Republic*
Born approximation in the context of electron energy loss spectroscopy

P23 **Jonas Schlagin; Dennis F. Dinu; Thomas Loerting; Klaus R. Liedl** - *Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria*
Ab initio calculations of anharmonic vibrational spectra of carbonic acid and carbonic acid methyl ester

P24 **Jutta S. Schnizer, Magdalena Salzburger, Christian van der Linde, Martin K. Beyer, Milan Ončák** - *Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität Innsbruck, Austria*
Structure and spectroscopic properties of hydrated O_2^- and O_3^- ions

P25 **Gabriel R. Schöpfer; Ethan M. Cunningham; Martin K. Beyer; Milan Ončák** - *Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität Innsbruck, Austria*
Dissociation pathways of hydrated magnesium sulfate clusters $[Mg_n(SO_4)_{n-1}(H_2O)_m]^{2+}$

P26 **Renata Sechi; Tibor Höltz** - *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economic; Furukawa Electric Institute of Technology, Nanomaterials Science Group, Hungary*
DFT study of CO_2 activation on $Pd_xPt_{(4-x)}$ clusters in the gas phase

P27 **Ján Šimunek; Jozef Noga** - *Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Slovakia*
Running Hartree-Fock calculations in local molecular orbitals.

P28 **Karlo Sović; Ines Primožič; Tomica Hrenar** - *Department of Chemistry, University of Zagreb Faculty of Science, Croatia*
Conformational analysis of quinuclidin-3-one derivatives

P29 **Marek Štekláč; Lukáš Bučinský; Marián Gáll; Ján Matúška; Michal Pitoňák** - *Institute of Physical Chemistry and Chemical Physics FCHPT STU, Bratislava, Slovakia*
Potential inhibitors of SARS-CoV-2 proteases

P30 **Martin Šulka; Katarína Šulková; Matúš Dubecký** - *Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava Slovak University of Technology in Bratislava, Slovakia*
Assessing the accuracy of Quantum Monte Carlo in hydrogen-bonded and strongly correlated systems.

P31 **Katarína Šulková; Martin Šulka; Andrej Antušek** - *Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava Slovak University of Technology in Bratislava, Slovakia*
Exploring water adsorption and reactivity in a series of doped aluminum cluster anions

P32 **Ádám B. Szirmai; Bónis Barcza; Attila Tajti; Péter G. Szalay** - *ELTE, Eötvös Loránd Uninversity, Institute of Chemistry, Hungary*
Theoretical description of interacting chromophores

P33 **Nina Tokić, Tomislav Piteša, Marin Sapunar, Nađa Došlić** - *Faculty of Science, Department of Physics, Croatia*
What can we learn by comparing surface hopping algorithms?

P34 **Barbora Vénosová; František Karlický** - *Department of Physics, Faculty of Science, University of Ostrava, Czech Republic*
MXene quantum dots: Effect of surface/edge functionalization on their optical properties

P35 **D. Vrška, P. Neogrády, V. Kellö, M. Urban, M. Pitoňák** - *Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Slovakia*
Excited states of auro-carbons: CASPT2 and CCSD(T) calculations of C_2Au_2 and C_2Au_4

P36 **Maks Walewski; Matthew D. Frye; Michał Tomza** - *Faculty of Physics, University of Warsaw, Poland*
Quantum interference effects in cold Rb–Sr^+ collisions high above the ultracold regime

P37 **Aleksander P. Woźniak; Maciej Lewenstein; Robert Moszyński** - *Faculty of Chemistry, University of Warsaw, Poland*
Effects of electronic correlation on the high harmonic generation in helium

P38 **Bárbara Zamora; László Nyulászi; Tibor Höltzl** - *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Hungary*
DFT-based investigation of structure and CO_2 adsorption on zinc dopped copper clusters

Invited Lectures

A Mystery of a Through-Space Indirect NMR Spin-Spin Coupling Between Two Hydrogen Atoms

Olga Malkin

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia
email: olga.malkin@savba.sk

Indirect nuclear spin-spin coupling constants are amongst the most important magnetic resonance parameters, invaluable in establishing molecular structure from NMR spectroscopy. Their detailed understanding in terms of molecular and electronic structure is thus of central importance in many fields of research and has been pursued since the beginnings of NMR spectroscopy. Nowadays quantum-chemical calculations can offer a variety of tools for the interpretation of couplings including visualization of spin-spin coupling pathways by real-space functions. [1]

In this presentation we show how visualization of NMR spin-spin coupling pathways has been used for interpretation of the experimentally detected "through-space" indirect spin-spin couplings between protons formally separated by 18 covalent bonds. [2] Usefulness of methods of deductive reasoning for the explanation of the newly observed phenomenon is demonstrated. [3]

Acknowledgment: This work received funding from the Slovak Research and Development Agency (grants APVV-19-0516) and VEGA (grant 2/0135/21).

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[1] O.L. Malkina, V.G. Malkin, Angew. Chem. Int. Edition 42, 4335 (2003)
[2] M. Dračínský, M. Buchta, M. Buděšínský, J. Vacek-Chocholoušová, I. Stará, I. Starý, O.L. Malkina, Chem. Sci. 9, 7437 (2018).
[3] Sir Arthur Conan Doyle, The Complete Sherlock Holmes, published by Barnes & Noble, Inc., 1122 pages (1992)

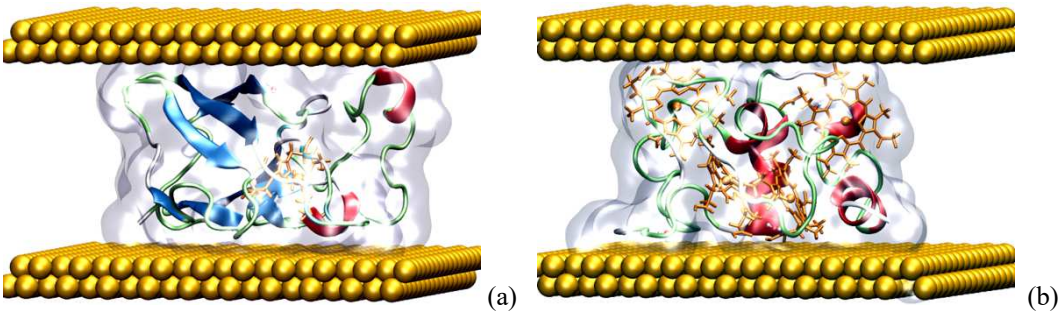
Electron Transport on Biomolecular Interfaces with Metal Electrodes

Zdenek Futera[a], Outi Vilhelmiina Kontkanen[a], Denys Biriukov[a,b]

[a] *Faculty of Science, University of South Bohemia, Branišovská 1760, 370 05 České Budějovice, Czech Republic*
[b] *Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 542, 160 00 Prague 6, Czech Republic*

Electron transfer facilitated by redox-active proteins is utilized in various biological processes, including photosynthesis, respiration cycle, or denitrification reactions. Blue copper proteins such as Plastocyanin or Azurin and the heme-containing cytochromes often participate in these redox cascades. Recently, these proteins started to be utilized in nanobioelectronic devices due to their suitable electron-transfer properties. However, non-expected physical phenomena were observed when the proteins were incorporated between metal contacts or electrodes. While in a native aqueous environment, the electron flow through the system of redox sites proceeds by the thermally activated hopping mechanism, the temperature-independent currents of relatively high magnitudes were detected on protein/metal junctions.[1,2] These data suggest that the electrons on the bio/metallic interfaces and junctions are transferred by the coherent tunneling mechanism, independently of the redox-active states.

We investigate these electron-transport phenomena by means of computer simulations based on classical molecular dynamics (MD) as well as the first-principles description within the framework of density functional theory (DFT).[3,4] While the incoherent hopping could be studied by combined quantum-mechanical / molecular-mechanical (QM/MM) techniques,[5] the coherent tunneling requires a quantum description of the whole interface models. Recently, we applied these methodologies on Azurin blue-copper protein and on small tetraheme cytochrome (STC), which were previously studied experimentally. We showed that the transport mechanism in both Azurin and STC junctions between gold electrodes is the coherent tunneling facilitated by conduction-band states of the proteins. In contrast to their redox properties in solution, the presence of the metal cations in the protein structures is not essential for their conductivity on the metal interfaces. The reason for this drastically different behavior in solution and on the metal interfaces is the significant electronic-level misalignment between the protein and metallic states.[6]



(a) (b)

Figure 1: Structure of (a) the blue-copper protein Azurin, and (b) STC gold junctions.

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[1] Garg, K. et al.: Direct Evidence for Heme-Assisted Solid-State Electronic Conduction in Multi-Heme c-Type Cytochromes. *Chem. Sci.* 9, 7304 (2018).
[2] Futera, Z. et al.: Coherent Electron Transport across a 3 nm Bioelectronic Junction Made of Multi-Heme Proteins. *J. Phys. Chem. Lett.* 11, 9766 (2020).
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SPECTRAL SIMULATIONS FOR BIOINORGANIC CENTERS: IN THE EYE OF THE BEHOLDER

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For relatively large bioinorganic centers, such as hemes, vitamin B_{12}, or the FeMoCo iron-sulfur-molybdenum cluster of nitrogenase, computational chemistry may be an obligate addition to experimental methods – especially when investigating short-lived species such as catalytic cycle intermediates. However, the large size of these systems, together with the gaps in experimental knowledge regarding their structure/purity/properties, make it particularly challenging to (1) apply accurate computational methods and (2) expect an accurate experimental benchmark. Nevertheless, a good number of reports will still claim excellent experiment-theory agreement and will thereby confuse anyone approaching the field from the outside.

Four case studies will be presented, all centered around efforts to unravel the reactivity of bioinorganic transition metal centers towards hydrogen peroxide: the non-heme iron enzyme superoxide reductase, the ferryl Compound II species of heme proteins (globins, peroxidases, cytochromes P450, catalase etc), the heme-iron-sulfur center of sulfite reductase, and the peroxide complex of cobalamin (vitamin B_{12}). [1-5]

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PUSHING MECHANISTIC STUDIES TO THE LIMITS. BUT IN WHICH DIRECTION?

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Mechanistic studies, based on rapidly evolving and widely available density functional theory methods, are among the most standard applications of computational chemistry. Even if these studies are performed routinely, accuracy is still essential due to the well-known exponential dependence of the rate constants on the activation free energies. Given that the free energies are dependent on multiple contributions with different error characteristics, it is important to identify their robustness concerning the applied methodology and approximations.
Based on real-life case studies from our research group (such as the isomerization of a fluxional natural product, and a reduction reaction catalyzed by a frustrated Lewis pair catalyst), we are going to demonstrate the relative importance of different free energy components, starting from the approximation of the electronic energies [1] up to the handling of conformational entropy [2]. By systematic inclusion and exclusion of these terms and the assessment of their relative costs, we are aiming to provide a recipe for optimal resource management.

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PHOTOCHEMICAL ORIGINS OF LIFE ELUCIDATED BY AB INITIO QUANTUM CHEMISTRY

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The question of the origins of life ignited imagination of the mankind since the dawn of its existence. It would be difficult to outline all the scientific hypotheses that were proposed regarding the abiotic synthetic routes that led to the formation of the first single-cellular organisms about 3.8 Gy ago. However, recently there is a growing evidence that all the building blocks of a protocell could form in a very similar system chemistries. The scenario proposed by Sutherland and Szostak [1, 2] involves streams flowing down the slopes of an impact crater, leaching metals and prebiotic feedstock molecules like cyanides under intense ultraviolet radiation. The latter seems to be crucial and leads to interesting photochemical transformations, necessary to produce nucleotides, aminoacids, simple sugars and lipids – all that is required to form a protocell. In this contribution an overview of the photochemical processes driving these reactions, as elucidated by ab initio quantum chemical calculations [3, 4, 5, 6], shall be discussed.

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QUANTUM CRYSTALLOGRAPHY. AN OVERVIEW, AND ISSUES RELATED TO THE PRESENCE OF HEAVY ELEMENTS.

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Quantum crystallography (QCr) [1] 'is established as the discipline where quantum-mechanical methods and computational chemistry combine with X-ray, neutron or electron scattering techniques to gain a better understanding of crystalline material properties' [2, 3]. Diffraction intensity from X-ray scattering experiments are given as a square of structure factors. Structure factors are the Fourier transform of electron (charge) density and this is exactly where quantum chemistry (electron density) meets crystallography (a periodic lattice which causes the diffraction of the incident X-ray beam).

The first part of the lecture will deal with the introduction of the crystallography concepts when retrieving the experimental charge density from the measured structure factors, i.e. the multipolar model [4]. The second part of the lecture will give a compilation of instances of the synergy between quantum chemistry and crystallography [5]. The third part of the lecture will be devoted to relativistic quantum crystallography, such as the extraction of relativstic effects, and the radiation damage present in compounds containig mercury [6].

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INVESTIGATING SUNLIGHT-TRIGGERED EXCITED-STATE DYNAMICS OF TRANSIENT ATMOSPHERIC MOLECULES

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Volatile organic compounds (VOC) are ubiquitous atmospheric molecules which generate a complex network of chemical reactions in the troposphere, often triggered by absorption of sunlight. Since the short lifetime of some transient VOCs poses significant challenges for accurate experimental and spectroscopic measurements, there is an urgent need for predictive computational approaches to study photochemistry and photophysics of VOCs.

We show how recent advances in computational photochemistry allow us to calculate *in silico* photolysis rate constants.[1] Such rate constants are utilized in general atmospheric models used to predict the accurate composition of atmosphere but are often not experimentally available for transient VOCs. Photolysis rate constants depend on three key pieces of information: the flux of the radiation source (sun/laser), the photoabsorption cross-section of the molecule and the wavelength-dependent photolysis quantum yield. We show how one can evaluate the sought-for ingredients – and consequently the corresponding photolysis rate constants – by combining state-of-the-art electronic structure methods and nonadiabatic molecular dynamics methods. We also analyze and compare different approaches for computing photoabsorption cross-sections of VOCs[2] and evaluate reliability of different ways to estimate quantum yields[3].

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Complex Absorbing Potential Based Coupled Cluster Method for Resonance and Decay

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Following Cizek's seminal paper on coupled-cluster theory [1], several new developments have taken place for energies, analytic gradients and derivatives, in general, making CC theory gold standard of quantum chemistry. The developments have also included multi-reference variants, alternate forms of CC theories, equation-of-motion based CC theory.

In this talk, I will highlight work from our group on new developments of inclusion of complex absorbing potential (CAP) in CC theory such that unbound states, like resonant and several decay states, like inter-atomic coulombic decay and Auger decay, can be easily described. Some recent results from both these developments will be presented. As a novel application, resonant excited states of SO_2 anion will be presented using CAP multi-reference CC theory

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To infinity, and beyond: expanding the *on-the-fly* NAMD capabilities for modeling cutting-edge photophysical phenomena

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In my talk, I will describe our recent efforts to extend capabilities of the *on-the-fly* nonadiabatic molecular dynamics (NAMD) towards covering new complex photochemical and photophysical phenomena. This specifically includes time-delayed multi-photon excitations and single-photon molecular emission, the latter work being performed in direct cooperation with prof. Daniel Escudero and his team at KU Leuven.

The time-delayed multi-photon excitation techniques have recently gained attention as a powerful tool to control direction and enhance efficiency of several fundamental photoreactions, including photo-cycloreversion of diarylethene molecular switches [1] and photo-oxidation of water [2]. Despite the well-confirmed enhancement effects observed in experiment, providing comprehensive theoretical description for so complex photo-processes poses a high challenge and, in most cases, cannot be achieved without inclusion of the dynamic nonadiabatic effects.

On the other side, single-photon emission plays a fundamental role in modern quantum information technology [3]. From the photophysical point of view, a molecule may act as a reliable single-photon emitter under a delicate balance of slow nonradiative and ultrafast radiative deactivation pathways. However, possibilities for theoretical modelling of these processes on equal footing and on sufficiently long timescales has been very scarce until now.

Our developed modifications to the Tully surface hopping (TSH) algorithm, covering the multi-photon effects and surface-hopping radiative deactivation have been recently implemented in the semi-empirical quantum chemistry package MNDO99 which allows for high-quality and very time-efficient NAMD propagations.

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UNUSUAL NON-SPHERICAL DELTAHEDRA IN METALLABORANE STRUCTURES

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Polyhedral boranes with only boron and carbon vertices generally have structures based on the spherical so-called *closo* deltahedra in which the vertices are as similar as possible and all faces are triangles. Degree 4 and 5 vertices are typically found in such deltahedra having less than 12 vertices. However, the most spherical 11-vertex deltahedron has a single degree 6 vertex. For deltahedra with more than 12 vertices degree 6 vertices become more common. Most spherical deltahedral boranes with n vertices typically have $2n + 2$ skeletal electrons as determined by the Wade-Mingos rules [1, 2]. Replacing some of the boron and/or carbon vertices in such deltahedra by transition metal moieties can lead to deviations from sphericality in the energetically preferred structures since transition metal moieties, particularly those of the second and third row transition metals, energetically prefer higher degree vertices than boron and carbon atoms. The smallest such deviations from sphericality in metallaboranes occur in the so-called *isocloso* structures having more degree 6 vertices for transition metal moieties than the corresponding *clos*o structures with the same number of vertices. Density theory studies show that 10-vertex systems, in particular, favor the C_{3v} *isocloso* structure in systems with 20 Wadean skeletal electrons (=$2n$ for n = 10) in contrast to an isomeric D_{4d} *closo* bicapped square antiprism structure [3].

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BUILDING POTENTIAL ENERGY SURFACES *on-the-fly* BY DEEP LEARNING.

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Potential energy surfaces determine the spectroscopic properties and dynamic behaviour of molecular systems. An accurate representation of potential energy surface (PES) requires numerous energy evaluations for different configurations of the investigated system. Although the number of evaluations can be reduced by using some type of PES expansion, it still demands generation of many grid points where energy will be evaluated.[1, 2] Construction of PES using deep learning has grown significantly due to the release of several software packages and improved algorithms and hardware. However, building PES is far from trivial, starting from a dataset selection, proper coordinates determination, coverage, using the correct setting in the learning method, *etc*.
Deep learning applied to *on-the-fly* molecular dynamics data has been utilized for building of PES for single molecule systems. Training set for each molecule consisted of energy values sampled from PES spanned in particular set of distance coordinates. These coordinates have been previously determined by machine learning protocol using tensor decomposition of molecular dynamics trajectories and cover more than 90% of the total variations in geometries. At each learning cycle, the training set was gradually increased, and the neural network was trained on this new set and compared with the previous best network.[3] Back-propagation algorithm was used to train the network, and the regression accuracy was monitored and used as a criterion during learning.

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Bonding Between Molecular Fragments Shows the Flaws of Persistent Pre-Quantum Chemistry Models

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A Molecular Isodensity Contour, MIDCO, is a closed surface $G(a)$ of some constant electron density value a in a three-dimensional molecule. These two-dimensional MIDCO surfaces $G(a)$ in three dimensions are analogous to the one-dimensional contour lines $L(b)$ representing equal-height points of some constant elevations b describing a mountainous terrain on a two-dimensional map.

Such MIDCOs, with an appropriate range of electron density value a, collectively provide a precise, and detailed description of molecular electron distributions. Hence, MIDCOs also give a precise description of actual chemical bonding, far beyond the early, pre-quantum-chemistry bond models, where actual bonding has been imagined only between neighbour atoms, leading to the traditional structural formulas.

As long as electron density in a molecule has been assigned only to individual atoms, this model has appeared fine, however, quantum chemical analysis of electron densities has shown that in a polyatomic molecule, of, say, 16 atoms, various MIDCOs may enclose more than one nucleus, say, 2, or 5 nuclei, and of course, some others enclose all 16 nuclei.

Imagine a MIDCO $G_{rst}(a)$ enclosing the 3 nuclei r,s,t, and a non-overlapping other MIDCO, $G_{uv}(a)$ enclosing the 2 nuclei u, v, where these MIDCOs may appear as two, separate, "quasi-autonomous" regions, close to one-another within the molecule. If the density threshold a is decreased, these two MIDCOs may merge into a single new MIDCO. In fact, very similar relations may exist between the original MIDCOs, than those relations between the two MIDCOs $G_x(a')$ and $G_y(a')$ of high density threshold a', each enclosing just one nucleus, x, and y, respectively, which nuclei may be actual neighbors, with traditional "bonds" within the molecule. Here, a decrease of the threshold value a' leads to a merger of these two MIDCOs within a larger MIDCO, indicating a chemical bond !

Indeed, the same type of actual relation exists between the two atomic groups r,s,t, and u,v. That is, chemical bonding is not confined to atom pairs, but there are very similar electron density features indicating "bonding" between two polynuclear fragments within a molecule.

The MIDCO model provides a justification to review the traditional bonding ideas rooted in pre-quantum chemistry times, and give proper considerations to the role of bonding between polynuclear fragments within a molecule.

P.G. Mezey "Fuzzy Electron Density Fragments in Macromolecular Quantum Chemistry, Combinatorial Quantum Chemistry, Functional Group Analysis, and Shape−Activity Relations" *Acc. Chem. Res.* 2014, 47, 2821−2827.

ANISOTROPY, LOCAL DISORDER AND POLYMORPHISM OF MOLECULAR CRYSTALS

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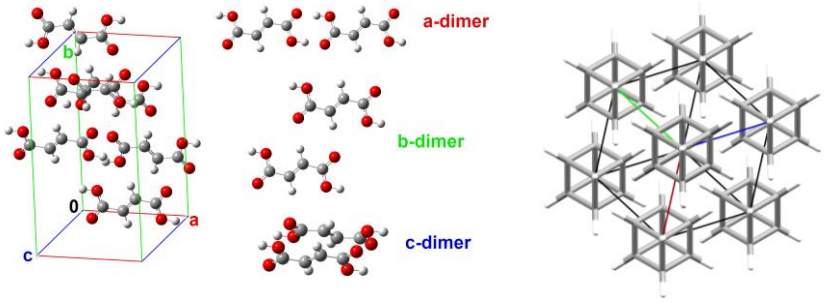
Molecular crystals are known for the delicate interplay of non-covalent interactions governing the molecular packing and cohesion. This work exploits first-principles methods to predict, quantify and interpret structural and thermodynamic phenomena related to two material classes – biogenic carboxylic acids and caged hydrocarbons. Going beyond the established methods for treatment of molecular crystals focusing on sublimation [1,2] or polymorphism [2], this works focuses also on phenomena such as local disorder and its entropy or local anisotropy.

The former exhibit a considerable anisotropy of their thermal expansion, which is interpreted using fragment-based calculations of the cohesion of these crystals. SAPT calculations are then used to decompose the pair interactions, and to identify the directions of the strongest cohesion, imposed by hydrogen bonding, restricting the thermal expansion. In addition, two polymorphs are currently known for each of succinic acid, fumaric acid and malic acid with various ambiguities on their experimental ranking. Quasi-harmonic DFT calculations, refined with the ab initio fragment-based cohesive energies and a first-principles model of the configurational entropy, related to the static disorder of carboxyl protons is used to rank these polymorphs in silico.

Numerous caged hydrocarbons form relatively stable solid phases despite the large strain that these molecules often experience due to the bizarre geometries of their carbon skeletons. Compactness and high symmetry of these molecules enable very efficient crystal packing, which translates to unprecedentedly high densities and weakens the anisotropy of some of these materials. Uniform molecular surroundings then facilitates dynamic disorder in such crystals, which manifests as large-amplitude anharmonic molecular motions. The one-dimensional hindered rotor model is used to quantify the entropy associated to such anharmonic libration or rotation degrees of freedom. Finally, quasi-harmonic DFT calculations are used for predictions of the sublimation equilibrium, including also the contributions from the dynamic disorder.



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Predicting Reactivity and Selectivity of Transition-Metal Catalysts - Improving Accuracy Beyond Electronic Structure Theory

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Being able to quantify the factors that govern reactivity and selectivity in transition-metal catalysis is an ultimate goal for the prediction and rational design of superior catalysts. However, the success ultimately depends on the accuracy of the employed computational methodology. Besides the choice of the electronic structure method, identification of the most stable conformer or of explicit solute-solvent interaction are key to correctly predict molecular structures and free energy reaction pathways.
To determine the conformations of transition-metal catalysts is still a challenge due to their flexible ligand sphere and require tailored approaches based on the type of metal and ligand. Two different multiscale protocols will be discussed at the example of a Mo imido alkylidene *N*-heterocyclic carbene catalyst for olefin metathesis [1] and at the example of a supramolecular Cu-calixarene complex, catalyzing C-N and C-S bond formation.[2]
In addition, an approach to quantum chemical microsolvation is presented, where the number, position, and orientation of the solvent molecules is explicitly defined based on solvation thermodynamics. [3]

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Oral Lectures

HIGH-LEVEL COUPLED-CLUSTER METHODS WITH TENSOR DECOMPOSITION

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We report a complete implementation of the coupled-cluster method with single, double, and triple excitations (CCSDT) [1, 2] and CCSDT(Q) perturbative correction [3], where tensor decompositions are used to reduce the computational costs. For the coupled-cluster triple and quadruple amplitudes tensor we employ the Tucker compression [4] format, for example

$$t_{ijk}^{abc} = t_{XYZ}\, U_{ia}^{X}\, U_{jb}^{Y}\, U_{kc}^{Z}, \tag{1}$$

where the quantities U_{ia}^{X} are obtained from higher-order singular value decomposition (HOSVD) of an ap- proximate triple amplitudes tensor [5]. The central tensor t_{XYZ} is obtained as a result of the coupled-cluster iterations [6, 7]. The efficiency of the method relies on the fact that the optimal size of the SVD subspace (the length of the summation over X, Y, Z) sufficient to obtain a constant relative accuracy in the correlation energy scales linearly with the size of the system. Combined with proper factorization of the coupled-cluster equations this leads to N^6 scaling of the computational costs of the SVD-CCSDT method, compared with the N^8 scaling for the conventional (uncompressed) CCSDT. The (Q) correction can be evaluated with N^7 cost [8]. The method is chemically accurate and even more demanding levels of accuracy, such as 0.1 kJ/mol, can be obtained with a reasonable size of the SVD subspace.

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ON AROMATICITY AND ELECTRONIC PROPERTIES OF SELECTED ORGANIC MOLECULES: A THEORETICAL STUDY OF RELATION BETWEEN THE TWO

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Aromaticity is a property closely tied to studies of electronic properties of organic molecules, for example see **Fig. 1**. As it has no unified definition, many aromaticity indices were developed. But, since each of these aromaticity indices is based on different properties of molecules, it is difficult to fully assess aromaticity of molecule [1]. From among properties of molecules, magnetic, structural and energy properties can be used as guidelines for determination of aromaticity [2]. Aromaticity indices were developed on basis of these criteria [3-5], but they are also not unified. Some of these indices are standardized to scale from 0 to 1, e.g., Harmonic Oscillator Model of Aromaticity (HOMA) [6], and other provide exact values related in example to magnetic shielding, Nucleus-Independent Chemical Shift (NICS) index [7]. So, based on collected information, we have selected some aromaticity indices and electronic properties of known aromatic molecules and we have studied the relation between those properties. As there are various NICS indices, they show correlation in their values to some extent but not as much with some other aromaticity indices.

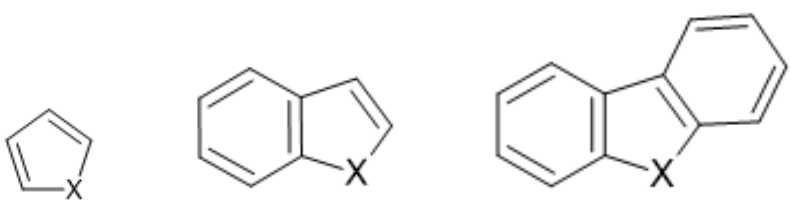

Fig. 1 Schematic of molecular structure of selected group of aromatic molecules

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PROBING DISORDERED PROTEINS' PHASE SPACE OF NMR CHEMICAL SHIFTS WITH FRAGMENTATION AND MACHINE LEARNING

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Theoretical chemistry has been utilized in protein structural classification for decades with many cutting edge advances. Proteins without well-defined 3D structures are extremely challenging for experimentalists due to their stochastic disordered nature many of which play roles in incurable maladies such as Tau proteins (Alzheimers') and amyloid proteins aggregations (Parkinson's).[1] Evidence has emerged pointing to the role of phosphorylation in the function of such intrinsically disordered proteins (IDPs). Few investigations have sought an in-silica approach to understanding these structures, as computations are prohibitively expensive and the proteins inherent disorder pose difficulties. Even fewer studies focus on the essential phosphorylation sites.

In this work we present our solution through a combined MD/ADMA/ DFT approach to computing NMR CSs for 31P, 15N, 13C, and 1H of IDPs. Disorder is simulated using a 1 μs molecular dynamics (MD) trajectory. Each selected frame was fragmented using the adjustable density matrix assembler (ADMA) considering only local influences within the molecule. Each fragment are optimized and computed for their NMR using density functional theory (DFT) calculations at the quantum level. We find strong agreement between the experimental CSs and those obtained using our computational scheme. Additionally, thanks to developments of machine learning, we implemented a cluster analysis technique known as the k+1 nearest neighbor approach based on the trajectory RMSD, and generated clusters of frames 10 times smaller than those used in the traditional step size approach. These clusters were able to identify group patterns within the phase space, drastically reducing the time for computation, with no loss in fidelity to experimental values. The inclusion of this method shows a positive future for in-silica structural analysis and machine learning in theoretical chemistry.

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VIBRATIONAL CORRECTIONS TO NMR SPIN-SPIN COUPLING CONSTANTS FROM RELATIVISTIC FOUR-COMPONENT DFT CALCULATIONS

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High-precision calculations of molecular properties require taking into account vibrational corrections. This is particularly true of NMR properties: nuclear spin-spin coupling constants and nuclear shielding constant, being sensitive to geometry distortions.

The newly developed and implemented method for calculating zero-point vibrational corrections to the nuclear spin-spin coupling constants at four-component relativistic level of theory is based on perturbational approach and is fully numerical. To test the method calculations have been performed for the following systems:

- H_2X, where X = O, S, Se, Te, Po;
- XH_3, where X = N, P, As, Sb, Bi;
- XH_4 where X = C, Si, Sn and Pb.

In addition to this, in order to demostrate the versatility of the method calculations have been carried out for an acetylene derivative, $HC{\equiv}CPbH_3$.

The main goal was to study the influence of relativistic effects on ZPV corrections and, thus, results calculated at relativistic and nonrelativistic approaches have been compared. The effects of relativity on ZPV corrections to spin-spin coupling constants are visible for the systems containing lighter elements (for example selenium and germanium) than the spin-spin coupling constants themselves. In the case of molecules containing heavier atoms, for instance BiH_3 and PbH_4, relativistic effects play a crucial role on the results and approximating ZPV corrections by the non-relativistic results may lead to larger errors than omitting ZPV corrections altogether.

Benchmarking Computational Approaches for the Prediction of Molecular Properties Pivotal in Photocatalysis

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In this work, we provide a benchmark of DFT functionals for calculating UV-vis spectra together with an ensemble-inspired statistical approach to carry out TDDFT benchmarks. The comparison between experiment and theory is done by considering the full spectrum curves instead of taking only individual peak positions and heights. In this way statistics can be potentially applied to hundreds of points instead of to a few selected points for each molecule-functional combination. Two parameters have been employed to fit the theoretical spectra to the experimental ones: a Gaussian width to uniformly broaden the bands and a scaling factor to stretch or compress the calculated excitation spectra. This approach is showcased here for a set of recently developed organic photocatalysts, each containing 50-100 atoms and exhibiting absorption in the visible region. For these molecules DLPNO-CCSD calculations are also performed to obtain wavefunction-based prediction for comparison. Five different error metrics have been tested and found that all of them predict very similar trends. We found that overall the B2PLYP and M06 functional performs the best among the tested functionals.

Adsorption and photochemistry of a functionalized push-pull stilbene

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4-(N, N-Dimethylamino)-4'-nitrostilbene (DANS) is a modified stilbene with an electron-withdrawing and electron-donating functional group exhibiting a competition between two alternative deactivation processes: photoisomerization (radiationless) and fluorescence decay. An essential question is how the environment (e.g., gas phase, different solvents) influences the ratio between these two deactivation channels [1]. Previous investigations on similar molecular switches (azobenzenes) emphasized, for instance, the importance of solid-state surfaces and how the interaction with the surface changes the outcome of the photoreaction [2]. In this work, we consider the adsorption of DANS on amorphous silica to eventually acquire knowledge of the impact of a silica surface on the photoreaction of DANS. We perform first principles density functional theory calculations[3] to study how DANS adsorbs on the surface and which orientations of the molecule are preferred. Subsequently, we analyze the energetically most stable adsorption configurations structures to understand the essential interactions (e.g., hydrogen bonds, Van-der-Waals contacts, ...) between DANS and the glass surface, as these might affect the photoisomerization of DANS. Our results reveal the significant role of the nitro moiety which, through withdrawing electron density from the OH groups of the silica, strengthens interactions with the surface and hence determines the adsorption geometry on the glass. Finally, we inspect the excited-state potential energy surfaces both in gas phase and in the presence of the silica surface to shed light on the differences between the two distinct environments. The detailed investigation of the deactivation paths is crucial to clarify how the barrier for the photoisomerization changes and in what extent the glass increases or suppresses the probability for fluorescence decay.

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INSTANTON APPROACH FOR SIMULATION OF VIBRATION-ROTATION-TUNNELING SPECTRA OF MULTI-WELL SYSTEMS

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We present an efficient method for the calculation of vibration-rotation-tunneling (VRT) spectra in the systems with multiple minima that is scalable to the system sizes beyond reach of the exact quantum (QM) methods. The recently developed Jacobi fields instanton theory (JFI) [1] is used to calculate tunneling matrix (TM) elements within a matrix model approach. The method proceeds by determining the minimum action paths (MAP) between each pair of accessible minima. The semiclassical wavefunction is then calculated along the MAP and its harmonic neighbourhood and the TM element determined using Herring formula. The number of potential gradient evaluations is of the order of 1000. TMs obtained in this way are found to be in good agreement with the exact QM and experimental values for many systems and across a wide range of orders of magnitude. Combined with the VCI energies for single-minimum calculations, JFI produces VRT spectra of malonaldehyde in a quantitative agreements with the accurate MCTDH results. We also apply the method to study the splitting patterns in partially deuterated water trimers[2] with multiple minima at different energies.

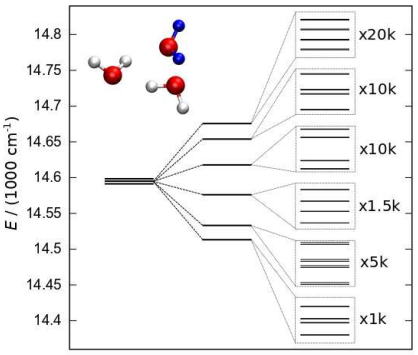

Figure 1: Splitting pattern of partially deuterated water trimer $D_2O(H_2O)_2$.

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DIABATIZATION OF ELECTRONIC STATES ALONG NONADIABATIC TRAJECTORIES

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Trajectory-based methods, such as Ehrenfest dynamics and surface-hopping dynamics, are widely used to simulate nonadiabatic reaction dynamics and to investigate the mechanisms of photoinduced molecular processes.[1, 2] When compared to the fully quantum approaches, their main advantage is that one can conveniently simulate the full-dimensional dynamics in the on-the-fly manner. However, while quantum dynamics is usually conducted in the diabatic basis, these methods traditionally employ the basis of the adiabatic electronic states, which often complicates the interpretation of the results.[3] This is due to the fact that the adiabatic states (unlike the diabatic ones) tend to significantly change their electronic characters along the nonadiabatic reaction path.

In this work, an efficient protocol for the diabatization of electronic states along the surface-hopping trajectories will be presented. Its performance will be illustrated on several famous photochemical systems. This will include the calculation of the surface-hopping diabatic populations and the decomposition of the time-resolved spectroscopic signals to the contributions of different diabatic transitions.

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SYMMETRY-ADAPTED PERTURBATION THEORY BASED ON MULTICONFIGURATIONAL WAVE FUNCTION DESCRIPTION OF MONOMERS

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We present a formulation of the multiconfigurational (MC) wave function symmetry-adapted perturbation theory (SAPT) [1]. The method is applicable to noncovalent interactions between monomers which require a multiconfigurational description, in particular when the interacting system is strongly correlated or in an electronically excited state. SAPT(MC) is based on one- and two-particle reduced density matrices of the monomers and assumes the single-exchange approximation for the exchange energy contributions. Second-order terms are expressed through response properties from extended random phase approximation (ERPA). The dispersion components of SAPT(MC) have been introduced in our previous works [2, 3]. The method can take advantage of the Cholesky decomposition of two-electron integrals. SAPT(MC) is applied either with generalized valence bond perfect pairing (GVB) or with complete active space self-consistent field (CASSCF) treatment of the monomers. We discuss model multireference systems including excited-state complexes of benzene, pyridine and peptide with the local exciton corresponding to the lowest $\pi - \pi^*$ and $n - \pi^*$ states [4]. Results for a dataset of high-spin open-shell dimers [5] are also presented.

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VARIATIONAL DIRAC–COULOMB APPROACH WITH EXPLICITLY CORRELATED BASIS FUNCTIONS

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The no-pair Dirac–Coulomb(–Breit) equation is solved using explicitly correlated Gaussian functions [1, 2, 3, 4]. The explicitly correlated basis set significantly improves the description of the electron correlation compared to e.g. determinant basis set, however, the positive-energy projection is more complicated due to the lack of the underlying one-electron picture. Therefore, several positive-energy projectors are examined to achieve and justify the parts-per-billion convergence of the energy providing a starting point for further comparison and developments in relation with high-resolution atomic and molecular spectroscopy. The no-pair Dirac–Coulomb energy is compared with perturbative results for atomic and molecular systems with small nuclear charge numbers and it reproduces the perturbative expressions [5] up to $\alpha^3 E_\mathrm{h}$ order.

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HE_3 INTERACTION POTENTIAL: ASYMPTOTIC BEHAVIOR OF THE POST-BORN-OPPENHEIMER CORRECTIONS

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General formulas were derived for the leading terms, vanishing like $r_{12}^{-t} r_{23}^{-u} r_{31}^{-v}$ where $t + u + v \leq 9$, in the long-range expansion of the relativistic and adiabatic corrections to the three-body non-additive interaction potential for a system comprising three atoms. The derivation involves two major steps. In the first step, operators defining the post-BO corrections were represented in the form of a multipole expansion. In the second step, the multipole expansions were inserted into formulas for energy corrections in double perturbation theory—first order in a given post-BO correction operator, and second or third order in the interatomic interaction operator. Using the angular momentum coupling techniques the resulting expressions were rewritten as products of two factors: an interaction constant Z depending solely on properties of the interacting atoms, and a geometrical factor W depending only on the relative positions of the three atomic nuclei. The geometrical factor for the leading term in the asymptotic expansion of most of the relativistic corrections (mass-velocity, one- and two-electron Darwin) and of the adiabatic correction has the well-known Axilrod-Teller-Muto form:

$$W \sim \frac{3(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)}{r_{12}^3 r_{23}^3 r_{31}^3},$$

while the leading term in the asymptotic expansion of the orbit-orbit interaction vanishes like:

$$W \sim \frac{5 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3 - 12\cos^2\theta_3}{2\, r_{12} r_{23}^3 r_{31}^3} + \text{c.p.}$$

The interaction constants Z were calculated for a system of three helium atoms at the full CI level of theory using large orbital basis sets. The complete asymptotic expansions derived in this work were then utilized in developing an analytical function representing the non-additive three-body interaction potential of helium. This function was used in calculations of the third pressure, acoustic, and dielectric virial coefficients for helium for a wide range of temperatures.

DIRECT OBSERVATION OF THE FASTEST ACID-BASED REACTIONS: COMBINING FEL EXPERIMENTS WITH *ab initio* THEORY

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The water molecule upon ionization forms a radical cation $H_2O^+\cdot$ that acts as an extremely strong acid. This cation can be experimentally studied in solution using pulse radiolysis e.g., in highly concentrated sulfuric acid [1]. The proton transfer reaction was predicted to be an ultrafast reaction by theory [2] and can be traced experimentally in liquid water e.g., via X-ray absorption spectroscopy [3]. Alternatively, one can take advantage of finite size clusters and explore the ultrafast dynamics using the reaction microscope approach. Here, the XUV pump-XUV probe combination allows us to directly map the proton transfer reaction and fragmentation [4].

In this talk, I will present our study on the dynamics of water dimer upon the ionization, considering different electronic states. We observe a strong dependence on the electronic state for the PT rates, ranging from tens to hundreds of femtoseconds. The higher the excited singly ionized state, the slower the PT. To simulate events after irradiation that are invisible to the experiment, we used semiclassical molecular dynamics approach [5] combined with multi-reference *ab initio* theory. I will also discuss events following the ionization of lower-lying electrons. Here, the coupling of electronic and nuclear motion plays a decisive role. The calculations are compared with recent experimental data both in time and energy domains.

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APPLICATION OF MODERN DENSITY FUNCTIONALS IN MODELING OF EXCITED STATES OF ORGANIC DYES

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Electronic structure theories can provide valuable insight into the absorption and emission of radiation, enabling a deep understanding of the excited-state properties. In particular, electronic structure calculations may play a key role in tailoring the specific properties of organic dyes, provided accurate approaches are used. Undoubtedly, time-dependent density functional theory (TD-DFT) is the most widely used theoretical approach enabling computation of the optical signatures and excited-state properties of dyes. Nevertheless, none of the known density functional approximations (DFAs) can satisfactorily anticipate a wide number of properties. Thus unceasing efforts are made to develop new DFAs, followed by assessing/comparing their predictive power with other already well-established functionals.

Herein, we present an extensive analysis of the predictive power of time-dependent density functional theory in determining the excited-state properties of two groups of important fluorescent dyes, difluoroboranes and hydroxyphenylimidazo [1,2-a] pyridine derivatives. The vertical excitation energies and dipole moments (in the electronic ground and excited states) of the aforementioned dyes were determined using the RI-CC2 method as our benchmark and compared with 18 DFAs. Performed study showed that MN15 strongly outperforms other DFAs in terms of determining the excitation energy. However, in the context of dipole moments, there is no single DFA that would equally accurately determine ground-state (GS) and excited-state (ES) dipole moments of both dye families. Nevertheless, MN15 generates the lowest μ_{ES} errors together with one of the most accurate μ_{GS}.[1]

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Accurate Anharmonic Partition Functions using Low-Cost Hamiltonians and Monte Carlo Integration

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There is a major ongoing drive to accurately predict thermochemical data for calculation of energy balances and reaction equilibria to better model atmospheric, industrial, and combustion processes. Contributions to these efforts tend to focus either on high-quality Hamiltonians for electronic energies or on models for the motion of nuclei. For the latter, most state-of-the-art models rely on the same, core process of approximations to tackle the common set of challenges posed when dealing with the potential energy surface (PES) of a sufficiently accurate, high-quality *ab initio* Hamiltonian. These involve fitting or calculating an approximate, often low-dimensional, relatively uncoupled nuclear model based on as few data as possible from the Hamiltonian, trading off coarseness in the nuclear model for greater accuracy in the electronic model. However, this can introduce major errors when predicting data for certain systems prone to fluctional motions.

Using a different approach opens up a new way to deal with nuclear motion that can more easily capture certain, coupled behaviors with which the methods rooted in the standard approach can struggle. Rather than create bespoke, localized approximations on-the-fly, one can use a PES of an approximate Hamiltonian to begin with but that is fast enough to be sampled broadly, *e.g.*, UFF [1], DFTB [2], or machine learning potentials. Then, one can numerically integrate it over thermally accessible regions to get full, classical partition functions. Finally, the Pitzer-Gwinn correction [3] can correct for quantum effects in these full partition functions, or, alternatively, anharmonic correction factors can be taken and transferred to RRHO results of an *ab initio* PES.

Configuration Integral Monte Carlo Integration (CIMCI) [4] is a new method taking this approach. It uses Monte Carlo integration and an enhanced version of MISER [5] recursive stratified sampling to perform the necessary high-dimensional integration. The few fluctional systems for which proper reference data is available show CIMCI performing very well. *E.g.*, UFF with CIMCI gives standard molar entropy correction factors for H_2O_2 that are better than M06-2X [6] with VPT2 and on par with M06-2X with explicit 1D hindered rotor handling; absolute standard molar entropies with UFF with CIMCI are also better than CCSD coupled cluster with RRHO.

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THE MECHANISM OF BIOMIMETIC NITROGEN FIXATION: INSIGHTS FROM QUANTUM CHEMISTRY AND MICROKINETIC MODELLING

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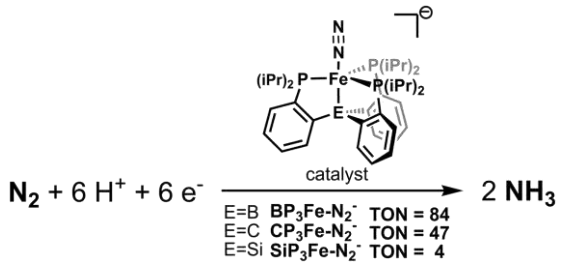
Synthetic Fe nitrogenases are promising candidates to mimic the function of the natural nitrogenase enzyme and to offer an environment friendly route aiming to fix dinitrogen by transition metal catalysts at room temperatures and atmospheric pressures, in order to produce ammonia and replace the energy consuming Haber-Bosch process. We used DFT calculations to investigate the catalytic mechanism of molecular nitrogenases (EP_3Fe, where EP_3 stands for the tris(phosphino)borate (E = B), tris(phosphino)alkyl (E = C) or tris(phosphino)silyl (E = Si) ligand) synthesized by Peters et al.[1] We discuss the catalytic cycle (the dinitrogen reduction reaction N2RR) of these complexes,[2] the possible side-reactions of hydrogen evolution reaction (HER)[3] and modes of deactivation. We propose that in the catalytic mixture an autocatalytic hydrogen evolution reaction (aHER) takes place which leads to consumption of substrates as well as catalyst deactivation.[4] Finally, we seek ways of avoiding the aHER reaction and improve performance through rational redesign of the catalysts.[5]



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AB INITIO STUDY OF THREE-BODY POLARIZABILITY OF HELIUM

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The trace of three-body polarizability tensor for helium was computed using the CC3 method. An analytic function representing the three-body isotropic polarizability was developed to correctly describe the known asymptotic behavior of polarizability for trimer configurations corresponding to both the three-atom and the atom-diatom fragmentation channels. We also developed a short-range function describing the local uncertainty of our calculations. Using both fits we calculated the classical and semi-classical (QFH) third dielectric virial coefficient (C_ε) for helium and its uncertainty. The results of our calculations were compared with available experiments and with classical and Path-Integral Monte Carlo (PIMC) calculations[1]. For high-temperatures we observed a significant discrepancy between the classical C_ε obtained using the superposition approximation[1] and *ab initio* polarizability (Fig. 1) due to the superposition approximation failure to properly describe short range behaviour (Fig. 2).

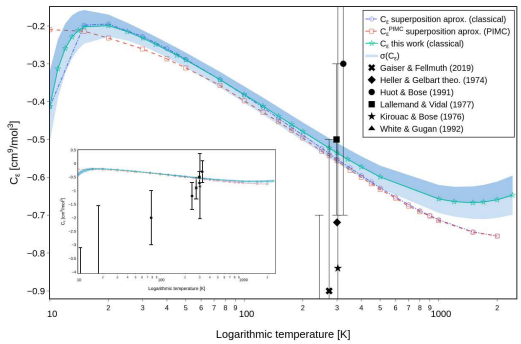

Fig. 1: Calculated third dielectric virial coefficient

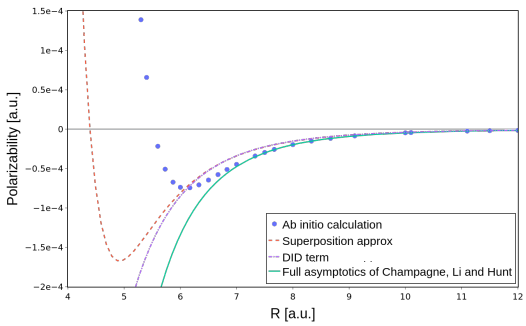

Fig. 2: 3-body polariz. of equilateral triangles

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AIMD SIMULATIONS IN MODELLING IR SPECTRA OF LIQUIDS

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Vibrational spectroscopy is commonly used to investigate interactions between molecules in a system of interest or to identify compounds in a sample with unknown composition. Predictions based on computational methods could be used to support the experiment, e.g. to identify individual bands observed experimentally or to predict possible shape of the spectrum. The most simple approach based on using quantum chemical calculations for isolated molecule in vacuum may provide some useful hints, but usually it is insufficient for condensed phase systems.

Our research concentrates on using molecular dynamics (MD) to model IR spectra of liquids, in particular systems that are used as electrolytes for batteries. Results obtained from classical MD are insufficient to reproduce spectra, so for this purpose ab initio MD (AIMD) is used. The IR spectrum can be obtained from the total dipole moment of the system as the Fourier transform of dipole moment autocorrelation function. More detailed information about contribution of different parts of the system to the whole spectrum is available from Fourier transforms of geometrical parameters such as bond lengths or angles.

In the presentation, examples of AIMD-based investigations of spectral changes induced by interaction will be shown. Discussed systems include Na salt in an ionic liquid[1] and Mg or Na/Li salts in organic solvents[2, 3]. The results show that the approach based on AIMD can satisfactorily reproduce the changes induced in IR spectra by solvent interactions with metal ions. As the last example, we will study the effects of hydrogen bonding on IR spectra of an ionic liquid with increasing content of water.

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OVERCOMING THE GAUGE PROBLEM FOR G-TENSOR CALCULATIONS IN THE FRAMEWORK OF FOUR-COMPONENT DFT

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The gauge problem or more precisely the gauge origin problem under Coulomb gauge has long been known as a confounding factor in the calculation of molecular properties related to external magnetic fields such as the NMR chemical shielding or the EPR g-tensor. The unclear choice of a common gauge origin render calculations irreproducible or at least incomparable. Not to mention that gauge dependency is inherently unphysical and therefore rarely conducive to experimental agreement except in the case of fortunate error cancellation. In chemical shielding, this is effect so significant that methods for distributed gauge origins which allow for well defined computational procedures have long been common practise. The most commonly applied[1] of those methods is the use of London orbitals[2] also known as gauge-including atomic orbitals (GIAO). In contrast, g-tensor calculations have been regularly performed with common gauge origins often placing the gauge origin at physically meaningful positions such as the centre of electronic charge or the centre of electronic spin-density. However, Ochsenfeld et al. demonstrated[1] that either approach for placing a coordinate system independent common gauge origin only provide reasonable results under very specific conditions.
Due to the high dependency of the electronic g-tensor on relativistic effects such as spin-orbit coupling unrestricted relativistic DFT provides a highly accurate and computationally efficient method to asses it[3]. We presented the first calculation of the EPR g-tensor in this framework including the use of GIAOs and explain from the relativistic point of view the origin of the gauge problem including its apparent negligibility under specific conditions. Thereby, we show for which cases the gauge problem becomes significant and provide a highly efficient and accurate method to eliminate it within g-tensor calculations.

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MASTER EQUATION MODELING OF BLACK BODY INFRARED RADIATIVE DISSOCIATION

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Black body Infrared Radiative Dissociation (BIRD) is molecular dissociation induced by the surrounding black body radiation in a low-pressure environment. Due to the shift of the black body spectrum with temperature, the respective dissociation rates are considerably temperature-dependent. We investigate BIRD combining Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) and Master Equation Modeling (MEM). Within MEM, one models explicitly photon absorption, photon emission and dissociation as a function of time, with the dissociation rate provided, e.g., from the RRKM theory. We employed the multiple-well approach that lets us model several reaction channels at the same time. However, the MEM scheme is versatile and may be easily extended to model Infrared Multiple Photon Dissociation (IRMPD) or processes following electronic excitation.

I will present our investigations on BIRD processes in two systems (Figure 1): a) The weakly-bound $CO_3^-.(H_2O)_{1,2}$ cluster present in the ionosphere. Here, water dissociation is observed, and MEM can be used for very precise modeling of water dissociation energies. b) Strongly-bound $[Mg_m(SO_4)_{(m-1)}(H_2O)_n]^{2+}$ clusters that serve as a model of sea-salt aerosols. Upon BIRD, they first lose water and then atmospherically relevant SO_3 molecules. Here, MEM gives us a deep insight into the energy stored in strongly-bound clusters in the form of latent heat.

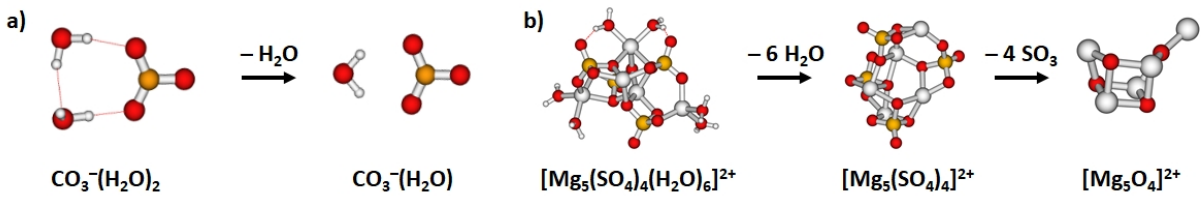

Figure 1: Black body infrared radiative dissociation processes observed in a) $CO_3^-.(H_2O)$; b) $[Mg_5(SO_4)_4(H_2O)_6]^{2+}$

SPECTROSCOPIC CONSTANTS FROM ROVIBRATIONAL CONFIGURATION INTERACTION CALCULATIONS

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Molecular (ro)vibrational spectra from microwave, millimeter wave and infrared experiments are usually represented by rotational and centrifugal distortion constants. These spectroscopic constants are derived from (and usually computed by) perturbation theory. In experiment, transition line lists are taken as reference for fitting an effective Hamiltonian, turning the constants into fit parameters. These constants (or parameters) concisely grasp the essence of a spectrum and, thus, are indispensable when it comes to communication of spectroscopic results.
While "experimental" spectroscopic constants are derived by fitting, their *ab initio* calculation is often based on vibrational perturbation theory (VPT). However, it is well-established that variational approaches, e.g., rovibrational configuration interaction (RVCI), are superior in calculating rovibrational states. Thus, spectroscopic constants from RVCI are desirable.
We here present a procedure, using RVCI [1] calculated rovibrational states and transitions as a reference for fitting Watson's A- or S-reduced Hamiltonian including up to sextic centrifugal distortion [2, 3]. Based on an educated parameter guess from VPT, our procedure becomes very efficient. First tests on small asymmetric top molecules (water, hydrogen sulfide, formaldehyde and thioformaldehyde) show very good agreement with experimentally derived spectroscopic constants [4].

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MODIFIED GRAPHENE QUANTUM DOTS AS HYDROGEN STORAGE DEVICES

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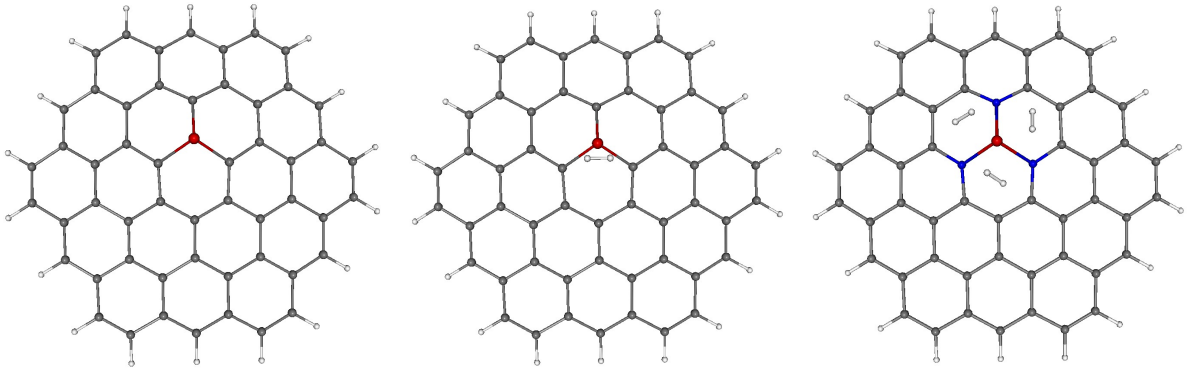
Hydrogen gas presents a clean and renewable energy source, having a potential to replace quickly consumed fossil fuels. One of the main issues of the process of obtaining hydrogen energy is the problematic storage of hydrogen gas under ambient conditions. Graphene quantum dots (GQDs) modified with transition metals (TMs) have already proved their capability to be used as H_2 storage devices [1, 2, 3]. Our DFT calculations, QTAIM and DOS analysis have confirmed the ability of the TM-doped GQDs to bind up to three H_2 molecules on one TM atom via η^2-dihydrogen interactions [3]. This ability can be further enhanced by the presence of N atoms in the vicinity of the TM [2]. In addition, our DFT calculations suggest that the H_2 binding performance of the TM-3N-doped GQDs can be altered by the oxidation and reduction, which can subsequently lead to the controlled H_2 release-and-capture mechanism.
A scheme of the selected modified GQDs under study is shown in Figure 1.



(*a*) (*b*) (*c*)

Figure 1: Fe-doped GQD (*a*), Fe-doped GQD plus H_2 molecule (*b*), Fe-3N-doped GQD plus three H_2 molecules (*c*).

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HOW TO APPLY MULTICONFIGURATIONAL THEORY TO IONIC SOLIDS?

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Modern quantum chemistry offers a large amount of accurate and reliable methods for computing the ground state and excited states in molecules. For the solid state the situation is quite different: periodic boundary conditions in connection to DFT is the dominating solution for all classes of compounds. DFT is often sufficient for ground state properties, but rarely for excited states. However, a combination of the following technological solutions might become a game changer: model potentials for cluster embedding [1]; compact basis sets [2]; advances in multiconfigurational theory; overall code performance improvement and parallelization.

We present our recent achievements in the modeling of the electronic structure of ionic metal oxides [1, 3]. Clusters are embedded in the layers of ab initio model potentials and point charges. We compared the properties of electronic structure against periodic calculations and investigated the convergence with increasing cluster sizes. Finally, some examples of multiconfigurational calculations (CASSCF/CASPT2) of electronic structure for point defects in ionic metal oxides ($Ni : MgO$, $Ce : YVO_4$) are discussed.

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ANALYTIC GRADIENTS FOR LOCAL DENSITY FITTING HARTREE–FOCK AND KOHN–SHAM METHODS

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We present analytic gradients for local density fitting Hartree–Fock (HF) and hybrid Kohn–Sham (KS) density functional methods. Due to the non-variational nature of the local fitting algorithm, we use the method of Lagrange multipliers to avoid the solution of the coupled-perturbed HF and KS equations. We propose efficient algorithms for the solution of the Z-vector equations and the gradient calculation, which preserve the third-order scaling and low memory requirement of the original local fitting algorithm. In order to demonstrate the speed and accuracy of our implementation, gradient calculations and geometry optimizations are presented for various molecular systems. Our results show that significant speedups can be achieved compared to conventional density fitting calculations without sacrificing accuracy.

THE FIRST SILVER CHLORIDE WITH RARE SILVER CLUSTERS FROM AB INITIO STUDY

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Apart from the oxides, where the silver clusters are part of extended silver sublattices, compounds with discrete subvalent $[Ag_6]^{4+}$ clusters appear extremely rare [1-3]. The new Ag_6Cl_4 resolved by performed evolutionary algorithms [4] carries all unique features of Ag^+ so far observed only in selected metal-rich oxides and as such represents an important addition to the discussion of the special bonding properties of silver with a filled d^{10}-shell. In this work we predict formation of subvalent octahedral $[Ag_6]^{4+}$ clusters for the first time as compound units in a simple binary subchloride Ag_6Cl_4 from ab initio simulations employing Density Functional Theory with improved Coulombic electron correlation (DFT+U) and exchange interactions (with hybrid DFT). The dispersive interactions (DFT-D3) were accounted for van der Waals Cl atoms interactions. The Ag_6Cl_4 as diamagnetic semiconducting silver subhalide is featuring stable and rare subvalent Ag_6 clusters with nominal $2e^-$–6c bonds coordination, including 1D argentophilic d^{10}–d^{10} intercluster interactions and 3D ionic connectivity enforced by Cl atoms [5]. Having appreciable formation enthalpy and dynamical stability as calculated by DFT in conjunction with the finite-displacement phonon method, Ag_6Cl_4 compound should be in principle possible to synthesize as a metastable phase relative to cubic AgCl phase.

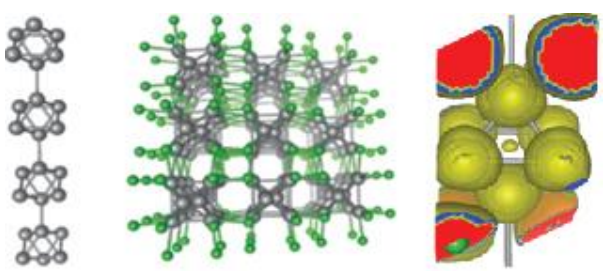

Figure 1. Left: fragment of Ag_6 octahedrons infinite 1D chain; middle: packing of the Ag_6 chains with bridging Ag–Cl bonds; right: electron localization function (ELF) for one Ag_6 octahedron with an additional small attractor inside.

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CHEMISTRY OF MXENE TERMINAL GROUPS AND THEIR EFFECT ON LAYER COHESION

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Mxenes as a new group of 2D materials have sprouted much interest due to their promising applications in energy storage and optical applications. Typical approaches to obtain single layer Mxenes employ intercalcation followed by sonication. These approaches often limit the size of obtainable single layer flakes. Specific functionalization of the surface can lead to decreased layer cohesion and a need for long sonication times and on the other hand increased cohesion can lead to more stable bulk Mxenes suitable for long term storage. Using a PBE-DFT approach with D3BJ dispersion correction we have obtained the exfoliation energies and equilibrium interlayer distances in bulk Mxenes of various types of T groups (-F, -OH, -O) on $V_nC_{n-1}T_x$, $V_nC_{n-1}T_x$, $Nb_nC_{n-1}T_x$ (n=1,3) in different ratios. The calculation of IR absorption spectra of these systems have also been preformed in hopes to provide a theoretical reference for their quantification using more accessible and cheaper methods.

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MECHANISMS OF ANTIOXIDANT ACTION OF PHENOLIC ACIDS AND THEIR CARBOXYLATE ANIONS

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Phenolic acids are naturally occurring antioxidants, which can be found in almost all plants and represent an important part of human diet. There are two main groups of phenolic acids: benzoic and cinnamic acid derivatives. Thanks to present OH groups, phenolic acids play the important role in the scavenging of free radicals [1]. The presence of methoxy group attached to the benzene ring may also affect their antioxidant properties [2].

Density Functional Theory study of eight benzoic acids and six cinnamic acids was performed. Thermodynamic calculations and geometry optimizations were performed using M06-2X [3] functional and 6-311++G(d,p) basis set [4, 5]. Solvent effect of water and benzene was described using SMD (Solvation Model based on the quantum mechanical charge Density of a solute molecule interacting with a continuum) approach [6].

Results of this study suggest that hydrogen atom transfer mechanism is operable in non-polar environment. However, low proton affinities propose preference of sequential proton-loss electron-transfer mechanism in polar ionization-supporting solvents, such as water, for both, parent acids and for their carboxylate anions. For non-dissociated acids at low pH, hydrogen atom transfer mechanism is also relevant. Moreover, calculated O–C bond dissociation enthalpies indicate that cleavage of O–CH_3 bond may affect radical scavenging activity [7].

Acknowledgement:
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BENCHMARKING ANHARMONIC VIBRATIONAL FREQUENCIES OF MOLECULAR DIMERS

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Accurate vibrational frequencies are crucial for the modeling of vibrational spectra and the calculation of Gibbs free energies. The anharmonic nature of individual normal modes as well as the coupling between modes can for instance be captured by second-order vibrational perturbation theory (VPT2) [1, 2]. While this approach is mostly used to describe rigid or semi-rigid isolated molecules, Howard *et al.* [3] have for instance shown that VPT2 calculations utilizing CCSD(T) yield also very good results for the water dimer and the HF dimer.

Herein, we assess the quality of VPT2 calculations for a diverse set of small molecular dimers, which are held together by dispersion interactions alone or also by intermolecular hydrogen bonds. To accurately capture all intermolecular interactions, we first utilize CCSD(T) for the whole set of dimers. Our so obtained VPT2 results are compared with available experimental data or high-level calculations of potential-energy surfaces. Problematic large-amplitude motions [2] like inter-/intramolecular rotations are described by one-dimensional hindered rotor models. Furthermore, we also discuss the accuracy of a simpler approach utilizing Morse oscillators. Then, we benchmark the quality of several density functionals in comparison to the CCSD(T) results. Later on, such an anharmonic approach can also be utilized for molecular crystals by embedding anharmonic monomer and dimer calculations into harmonic periodic calculations in a similar fashion as currently done for energies and geometries [4]. This might be crucial for crystal structure predictions, where numerous energetically similar polymorphs have to be ranked according to their Gibbs free energy [5].

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Visualization of EPR Hyperfine Structure Coupling Pathways

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Paramagnetic compounds represent an important class of technologically relevant materials. They can be used as contrast agents for enhancing NMR imaging, molecular magnets, materials for spintronics and advanced information storage, transition-metal battery materials and many others. Paramagnetic NMR spectra contain a wealth of information about paramagnetic compounds but their interpretation is often challenging. [1,2] One of the most interesting questions in the analysis of pNMR shifts concerns the pathways of the contact and pseudocontact shifts which help to understand the structure-property relations for paramagnetic compounds. [3]

In the present work we propose a new tool for visualization of hyperfine coupling pathways based on our experience with visualization of NMR indirect spin−spin couplings.[4] The plotted 3D-function is the difference between the total electron densities when the magnetic moment of the nucleus of interest is parallel and antiparallel to the external magnetic field and as such is an observable from the physical point of view. In contrast to the widely used visualization of spin density, our new approach depicts only the part of the electron cloud of a molecule that is affected by the interaction of the unpaired electron(s) with the desired nuclear magnetic moment. Implentation of the presented approach in relativisic framework allows one to visualize the spin-orbit effects on hyperfine coupling pathways.

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Poster section

ACCURATE EVALUATION OF COUPLED CLUSTER IONIZATION POTENTIALS AND ELECTRON AFFINITIES VIA EXCITATION ENERGY CALCULATIONS

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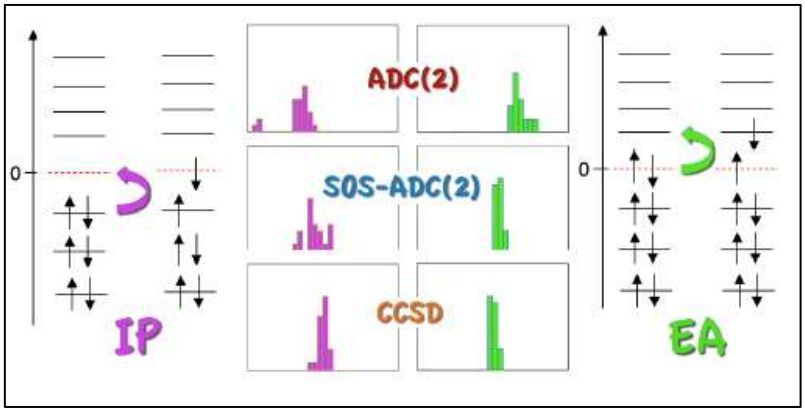
An alternative approach for obtaining accurate vertical ionization potentials (VIPs) and electron affinities (VEAs) via coupled-cluster excitation energy calculations is proposed. The concept allows a coherent handling of all ionic states, including ionizations from lower valence orbitals and attachments to higher-lying virtual ones. The use of existing, widespread quantum chemistry codes with minimal modifications makes the application of well-established wave function models possible, in full consistency with the treatment of charge transfer excitations. Among them, the spin-component scaled forms of the CC2 and ADC(2) methods are potent approaches, especially the scaled opposite-spin variants whose efficient implementations allow the handling of larger systems. The performance of several models is evaluated via benchmark calculations on various sets from previous works, containing small and medium-sized systems, including nucleobases. It is shown that with the most effective scaled approximate methods the accuracy of EOM-CCSD is achievable at a fraction of the computational cost, also outperforming many common electron propagator approaches.



A THEORETICAL STUDY OF THE OH-INITIATED ATMOSPHERIC DEGRADATION OF PENTACHLOROPHENOL.

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Properties, interactions and reactivity of molecules/ions related to anthropogenic activities during the last decades represent hot topic in atmospheric chemistry. Phytosanitary products such as pesticides/herbicides or oxides agents have impact on climate environment and quality of life [1, 2]. Pesticides/herbicides belong to partially Volatile Contaminants (VOC type) that can emitted to atmosphere during the application. Typical modes of their dissemination are wind erosion and/or evaporation from the surfaces after their application. Contamination of the environment by VOCs leads to health problems but can also cause disturbance of the balance in nature due to the volatility of the pesticides/herbicides those will enter the air after few days of the application.

This poster will present the results of our ongoing works for the pentachlorophenol compound using DFT and CASPT2 calculations to gain insight and characterize their atmospheric degradation processes unraveling which chemical molecules resulting from their decomposition could end up in the air in the gaseous state or in the form of aerosols.

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NMR shielding calculations of beta-NMR probe nuclei in ionic liquids.

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Beta-detected NMR is an ultrasensitive technique that is already well established in nuclear physics [1] and materials science [2]. The recent innovative introduction of ionic liquid targets opens the possibility of beta-NMR spectroscopy applications in chemistry [3], and accurate measurements of beta-NMR probe nuclear magnetic moments allow direct measurement of NMR shielding in beta-NMR experiments [4]. These experiments need extensive ab initio modeling support. We will present a computational protocol for NMR shielding of beta-NMR probe nuclei in ionic liquids, which is based on force-field molecular dynamics for solvation shell structure model and subsequent approximate models for NMR shielding. These models are based on non-relativistic coupled cluster and four-component Dirac-Kohn-Sham method. From benchmark calculations we can conclude that proposed NMR shielding models predict NMR shielding of ^{26}Na in ionic liquids with accuracy of few ppm [5]. The main sources of uncertainities will be discussed.

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COMPARISON OF DIFFERENT MODEL POTENTIALS FOR NON-COVALENT INTERACTIONS BETWEEN N-HETEROCYCLES IN GROUND AND EXCITED STATE

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We used multilevel methods to investigate the ground and excited states of non-covalently bonded chromophore dimers. We chose two coarse grained approaches: a QM/MM type electronic embedding, and a WFT-in-DFT type method. For both techniques, a high level coupled cluster calculation was carried out on one of the molecules, with the other modeled as the environment.

The ground state calculations were carried out on a pyrrole-pyrrole dimer in six different conformations and on a stacked cytosine-uracil complex. Based on these results we found that the QM/MM model lacked the exchange and dispersion interactions, while the WFT-in-DFT model had to be corrected only for the latter.

To create an accurate model, we used different combinations of model potentials available in the literature, such as the effective fragment potential (EFP2), an atomistic force field (GAFF) and DFT-D3 dispersion correction. We tested them against the results of the Symmetry-Adapted Perturbation Theory and the supersystem CCSD(T) calculations. The results showed that EFP2 components were superior over other potentials provided by the other methods. Hence, we augmented the original multilevel models with the appropriate EFP2 terms, and used them to describe the electronically excited states of the pyrrole-pyrrole and cytosine-uracil dimers in a stacked conformation.

These complexes exhibit Frenkel coupling, which was introduced through the transition dipole moment approximation (TDA). We calculated the PES of two coupled valence states for the stacked cytosine-uracil and pyrrole-pyrrole dimer, while four Rydberg excitations of the latter.

DEVELOPMENT AND ASSESSMENT OF QM:QM METHODS FOR MOLECULAR CRYSTALS

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In recent years, advances in method developments have been leading to increasingly reliable predictions of structures of molecular crystals. This has been highlighted by the impressive results in the prediction of possible crystal structures for organic molecules and, recently, also organic salts.[1]

Much of this progress can be attributed to the increased application of generalized gradient approximation (GGA) density functional theory (DFT) including dispersion models using periodic boundary conditions. We assess the available computational approaches for the revised X23b benchmark set of molecular crystals[2] using thermally-expanded structures which were calculated via the quasi-harmonic approximation. In addition, we introduce our own methods which are based on QM:QM (quantum mechanical methods embedded in quantum mechanical methods) schemes.[3, 4, 5] Using the latter approaches, we are able to approximate periodic results of hybrid functionals at a fraction of the computational time needed for the canonical methods. We will compare results for frequencies, cell volumes and geometries as well as lattice energies to the parent hybrid functionals.

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DFT STUDIES OF DIMETHYL AMINO PHENYL SUBSTITUTED SILVER PHTHALOCYANINE

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Breloy et al. [1] investigated a novel visible-light absorbing silver dimethyl amino phenyl substituted phthalocyanine photoinitiator (dmaph-Ag(II)Pc, see Fig. 1) for free-radical and cationic polymerizations. Upon irradiation, the electron transfer reaction between the photo-excited states of dmaph-Ag(II)Pc leads to the reduction of Ag(II) to Ag(I) and generates simul-taneously the nitrogen-centered radical cation (dmaph-Ag(II)$Pc^{\bullet+}$). In the next step, Ag nano-particles and aromatic carbon-centered radicals are formed.

We investigate the electron structure of optimized geometries of $[dmaph\text{-}AgPc]^{q}$ complexes with charges q = +1 to -2 in the lowest (singlet or doublet) spin states using standard B3LYP-GD3/cc-pVDZ(-PP)/SMD($CHCl_3$) treatment. Excited state energies are evaluated using the time-dependent DFT method.

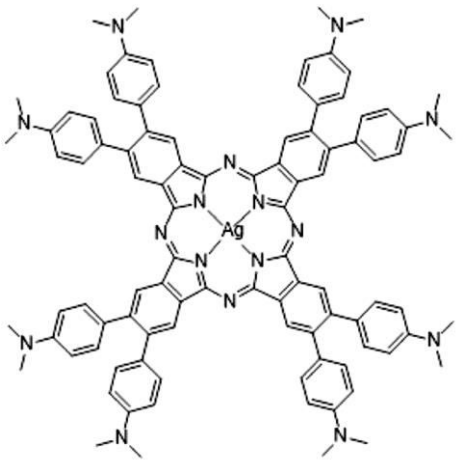

Figure 1. Structure of the neutral dmaph-Ag(II)Pc complex [1].

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RIGIDIZED 3-AMINOCOUMARIN FLUORESCENT pH PROBES FOR ACIDIC CONDITIONS

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Coumarins represent one of the most famous group of fluorescent probes, particularly due to their high quantum yields, excellent photostability, effcient cell permeation and low (cyto)toxicity. Herein, we describe rigidized small-molecule 3-aminocoumarin turn-on pH probes for low acidic conditions that allow rapid and effective yeast vacuolar lumen staining compared to commercial CMAC derivates. Focus of our work is on detailed understanding of the on-off switching mechanism using TD-DFT and ab initio calculations along with Franck-Condon analysis of emission profile.

PHOTODISSOCIATION OF SODIUM IODIDE CLUSTERS DOPED WITH 5-BROMOVALERATE

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Photochemistry of sea salt clusters is potentially relevant for atmospheric chemistry. Sodium iodide clusters $(NaI)_nNa^+$ investigated in mass spectrometric studies are usually much smaller than marine aerosols observed in the troposphere. Still, these mass spectrometric studies of sodium iodide clusters doped with organic molecules show a rich photodissociation behavior. Kinetics and analysis of the photodissociation products as a function of photon energy of these photochemical reactions provide insight into the ongoing reaction mechanisms.

Photochemistry of sodium iodide clusters doped with 5-bromovalerate, $Na_6I_4(BrC_4H_8COO)^+$, is investigated here. The clusters are produced via electrospray ionization and transferred into a Fourier Transform Ion Cyclotron Resonance (FT-ICR) cell where isolation of certain cluster sizes, photoirradiation and detection of product ions is performed. Clusters are isolated and irradiated with UV laser pulses and the photodissociation products are detected.

Observed fragments show clear evidence for a radical-triggered chemistry which involves C-C bond breaking. The proposed reaction mechanism starts with an attack of a Na radical splitting off the Br atom and ends with the attack of an I radical which finally leads to C-C bond breaking. The mechanism includes several transition states and the overall reaction is exothermic by over 2 eV. Quantum chemical calculations reveal details of the reaction mechanism.

PHOTOINDUCED CHARGE-TRANSFER PROCESSES IN CESIUM IODIDE CLUSTER IONS

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Charge-transfer processes resulting from excited states raise many questions such as where the electron moves to and whether it is localized around an atom or delocalized over the whole molecule. Alkali metal-halide clusters are well suited to study these phenomena and therefore act as a model system for a molecular understanding of this fundamental reaction playing a key role in many areas of science and technology.

Here, I investigate photoinduced charge-transfer processes in cesium iodide cluster ions using ground state and excited state quantum chemical approaches. We measured ions using a Fourier Transform Ion Cyclotron Resonance (FT- ICR) mass-spectrometer as the clusters were probed through irradiation with a UV- laser. The results show absorptions starting at about 270 nm and dissociation exhibits statistical nature, following a $[CsI]_n$ pattern. An exception is $[CsI_2]^-$, as there the fragmentation results in iodine radicals.

To better understand the nature of the involved processes, I computed the minimum energy geometry, UV- absorption spectra, natural transition orbitals, and dissociation channels of $[CsI_2]^-$ and $[Cs_{n+1}I_n]^+$ n=3-6 clusters using a DFT/TDDFT method. Further, with the help of a CASSCF calculation for the $[CsI_2]^-$ anion, I showed the importance of spin-orbit contribution considerations for systems containing iodine, as the ground state energy shows a significant shift of 0.3 eV if taken into account.

VIBRATIONAL AND ELECTRONIC SPECTROSCOPY OF $(C_{60})_n^{\pm}$-CLUSTERS.

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While for the IR-Spectra of $C_{60}^{0,\pm}$ there is already a quite good understanding, there is very little knowledge about C_{60} ions combining to clusters. But these clusters may be also of great interest, be it for astro-spectroscopy or also in technology like organic photovoltaic. In the experiment, helium nanodroplets are doped with clusters of $(C_{60})_n^{\pm}$ and after scattering on a surface, the abundance distribution of the clusters is recorded with a time-of-flight mass spectrometer [1].

In my work, I model $C_{60}^{\pm}$-clusters up to $C_{240}^{\pm}$ by using DFT calculations with GPUs and the TeraChem software. The use of GPUs allows a significant increase in calculation speed. The results are compared with other methods and bases for benchmarking as well with the experimental results of the IR spectroscopy.

I show that the optimization of the $C_{60}^{\pm}$-clusters works well with the GPUs and that it is a fast way to model different configurations of the clusters. We see that the vibration intensity for clusters increase strong in comparison to pure $C_{60}^{\pm}$ and we try to map the measured spectra to the vibrational spectras of the corresponding isomers which do not exceed $1600\,\mathrm{cm}^{-1}$. Also we show that first electronic transitions appear already below $3000\,\mathrm{cm}^{-1}$, which can not be found for pure $C_{60}^{\pm}$ where first symmetrically allowed electronic transitions are found at about $10\,000\,\mathrm{cm}^{-1}$ [2].

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DFT Analysis of Diels-Alder Reactions for the preparation of forskolin derivatives

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Diels-Alder reactions represent one of the most significant steps in the synthesis of forskolin derivatives. The cycloaddition in question takes place between a structurally invariable diene (tert-butyldimethylsilyloxybuta-1,3-diene) and a dienophile (methyl-p-benzoquinone) characteristically substituted in *meta-position* with respect to the methyl group. Depending on the nature of the substituent, individual stereoisomers of products are formed in various ratios. The presented theoretical study focuses on the calculation of reaction energy profiles for a set of substituted dienophiles. Trends in activation barriers are in good agreement with experimental stereochemical outcomes. Relative energies of transition states are interpreted in terms of orbital interactions between diene HOMO and dienophile LUMO. Both energy differences and frontier orbital compositions within the Mulliken population analysis are considered, with a straightforward correlation to the heights of activation barriers in the cycloaddition reactions.

Calculations of activation barriers were carried out at the B3LYP/6-31G* or B3LYP/6-31+G* levels of theory using the SMD implicit solvatation model within the Gaussian09 or Gaussian16 implementation. Comparative energy profile calculations and all orbital analyses have been done at the B3LYP/STO-DZ level using the ADF package.

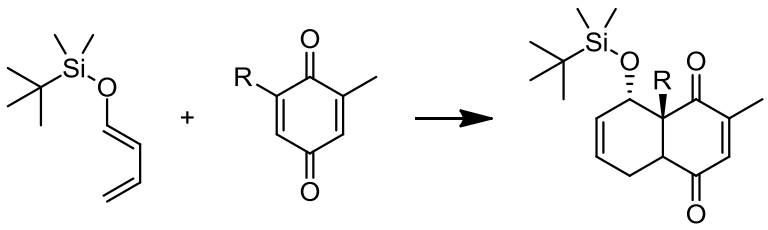

Figure 1. General scheme of Diels-Alder reaction for the preparation of forskolin derivatives.

Understanding the Effect of the Transition Metal on the Properties of Cyclopentadienyl-stabilized 5,1,3,2,4-Metalladithiadiazoles

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Introduction

Sulfur-nitrogen chemistry has experienced a noticeable progression over the past years, and this is what drove the rise in popularity of inorganic sulfur-nitrogen rings. Dithiadiazoles, the five-membered sulfur-nitrogen (S_2N_2) rings, were the ones that attracted special attention, and that resulted in the knowledge we now have about their preparation, reactivity, and bonding. However, far less attention and interest have been invested in the study of metalladithiadiazoles, and more importantly, transition metal complexes with an S_2N_2 fragment. In our work, we tried to fill this gap by investigating more deeply the 5,1,3,2,4-metalladithiadiazoles that have a half-sandwich structure stabilized with cyclopentadienyl (Cp) ligands (we refer to these complexes as $CpMS_2N_2$).

Method and Results

Based on our results, we aimed to describe the bonding of the CpM fragment to the S_2N_2 ligand by relying on a combination of parameters ranging from bond lengths to natural atomic charges, Gibbs free energy changes, and orbital energies. We experimented with different transition metals with a goal to understand the binding mechanism involved. We show how the bond orders and Gibbs Free energies shift as we move along the d block in the periodic table, and how that

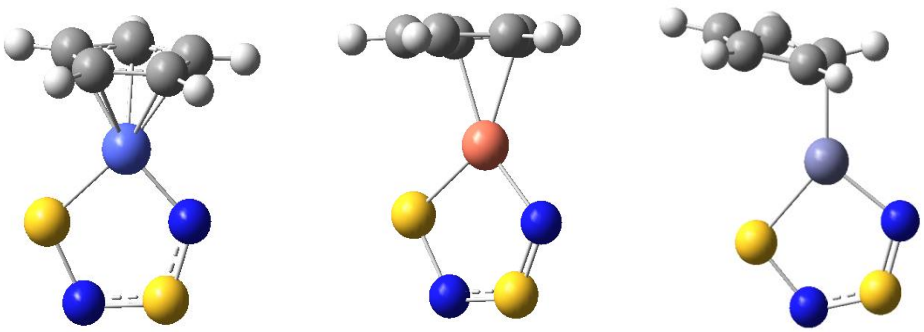

Figure 1 Change of Ligand Hapticity from η5 to η2 and η1

affects the hapticity of the ligand (from η^5 to η^2 and η^1 as seen in Figure 1).

We also try to interpret the change in aromaticity accompanied with the variation of the transition metal using magnetic and geometric criteria. Moreover, our calculations predict that besides the already synthesized cobalt compound, the vanadium and ruthenium compounds should be synthesizable as well.

EFFECT OF DUAL PHOSPHOPRYLATION ON THE ACTIVATION MECHANISM OF ERK2: COMPUTATIONAL INSIGHTS

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Protein Kinases (PKs) are considered to be the driving force for many cellular processes through transferring a phosphate group form ATP or GTP molecules to a specific substrate protein. [1] Ser/Thr and Tyr –specific kinases are two big groups that make up about 2% of the proteins encoded in the genomes of most eukaryotes. ERK2 (Extracellular-Regulated Kinase 2) is an important member of a signaling pathway that regulates cell growth and proliferation and is a target for cancer treatment. [2] ERK2 is activated by phosphorylation at the side chains of two amino acids, Threonine 183 (T183) and Tyrosine 185 (Y185). Upon activation, ERK2 enters the cell nucleus, where it carries signals involved in the regulation of cell proliferation and differentiation. Therefore, fundamental understanding of the control mechanisms for its activation and how specific mutations alter its activity may hold a promising prospect for cancer therapy.

In order to gain better understanding of the elementary effect of double-phosphorylation of T183 and Y185 on the ERK2 activity, we used two ATP-bound crystal structures of ERK2 (4GT3: unphosphorylated and 6OPG: phosphorylated). Phosphorylation might exert its effect via various routes, e.g. by changing the structure as well as influencing the electrostatic field. Therefore, we investigated the structural changes of the activation loop upon dual-phosphorylation using MD simulations. Furthermore, we carried out combined quantum mechanics molecular mechanics calculations (QM/MM) to study the effect of phosphorylation on the properties of the bound ATP-ligand. Analysis of atomic charges, molecular orbitals as well as bond orders and bond distances strongly suggest that phosphorylation weakens the O-P of the ATP ligand that is cleaved during the catalysis and thereby facilitates the kinase activity of the protein.

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ON QUANTUM CHEMICAL CALCULATIONS OF ACIDITY CONSTANT OF PHENOL DERIVATIVES AND THEIR CATION RADICAL FORMS

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Phenols and their derivatives are under interest for many decades due to occurrence in natural compounds and industrial products. They are obtained as intermediates in production of polymers, antioxidants surfactants and pesticides, as well as natural phytophenols and polyphenols [1].
The proper characterisation of chemical nature of phenol derivatives is essential for understanding chemical processes and reactions associated with these compounds. For this reason, we have studied different *o*-, *m*-, *p*- monosubstituted phenol derivatives from a theoretical point of view using quantum chemical methods employing density functional theory (DFT) method [2]. This method is currently one of the most widely used methods to calculate various thermodynamic quantities as has been shown in the study of similar compounds [3]. An important parameter in this type of calculations is the accurate selection of the solvent model, which can either include individual solvent molecules (explicit model) or describe the solvent environment in the form of an electrostatic cavity model (implicit model). In our case, we used an implicit model, which is less computationally and time consuming. This work focuses on the calculation of properties in strongly acidic environments, which is crucial, for example, for the reactivity of organic synthesis. The reaction scheme under study is presented in *Fig*. 1.

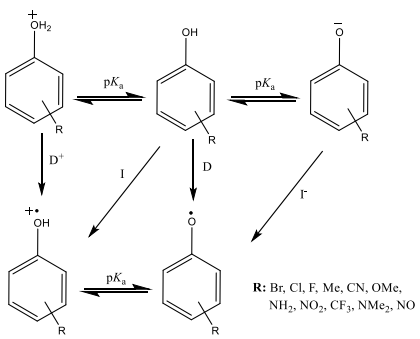

Figure 1. The scheme for studied molecules.

Acknowledgement
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A novel treatment of redundancy in Multi-Configuration Perturbation Theory

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Description of molecules having a predominantly Multi-Reference (MR) character has remained an open challenge for quantum chemistry to this day. A relatively straightforward way to treat such strongly correlated problems is to apply perturbative corrections to the MR starting function.
Multi-Configuration Perturbation Theory (MCPT)[1][2] is a simple approach in the family of MR-PT methods, where the unperturbed Hamiltonian is constructed in spectral form given by the MR function $|\Phi\rangle$ and various excited determinants $\{|\phi_k\rangle\}$. Zeroth-order energies are parameters that can be chosen in many ways, giving MCPT an appealing flexibility in tackling MR problems.
On the other hand, linear dependence of the zeroth-order states $\{|\Phi\rangle\} \cup \{|\phi_k\rangle\}$ is a well-known problem of MCPT. Previous solutions to the redundancy problem relied on selecting a principal determinant ("pivot"), which came at the price of introducing discontinuities along the Potential Energy Surfaces. The present approach circumvents this problem by treating all vectors of the redundant set on the same footing, using the concept of frames from linear algebra. This technique has been successfully used by us in the context of MR Coupled Cluster theory[3]. The resulting frame-based MCPT (fMCPT) is free of the pivot-dependence of previous MCPT models, while remaining a conceptually simple method.
In my talk I present the fMCPT formulae, and discuss the advantages and disadvantages of the formalism. Numerical performance of fMCPT is assessed on the example of bond dissociation and rearrangement processes, as well as calculation of singlet-triplet excitation energies, with strongly orthogonal and symmetry-broken geminal wave functions[4] used as reference.

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PREDICTION OF DOCKING SCORES TO THE MAIN PROTEASE M^{pro} BY MACHINE LEARNING

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The new coronavirus SARS-CoV-2 is the target of intensive research and drug development. Blocking of the main protease (M^{pro}) by drugs can compromise the virus replication. Extensive screening of the potential drugs to deactivate M^{pro} is time consuming even in the case of molecular docking[1]. Machine learning (ML) greatly reduces the time requirement [2]. The main concern that remains is the accuracy of ML. The 59,884 compounds from the ZINC database [3, 4] denoted as *in vivo* were docked against M^{pro} in AutoDock Vina 1.2.2 software [5, 6] using the AutoDock scoring function. The created database of compounds and docking scores was used to train, validate, and test three ML approaches. The first is TensorFlow (neural network), and the second is XGBOOST (gradient boosted decision trees) which both use the SOAP descriptor. The third is Deep Tensor Neural Network as implemented in the program package SchNetPack. The prediction capabilities of the proposed ML models were verified against a test database of 8983 compounds derived from original database. The influence of the docking score, charge, and size of the compounds on the accuracy of the prediction was investigated. Moreover, the calculation of uncertainty of NN's predictions was proposed.

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COMPUTATIONAL INSIGHTS INTO PHOTOCHROMIC BEHAVIOR OF IMINOTHIOINDOXYLS

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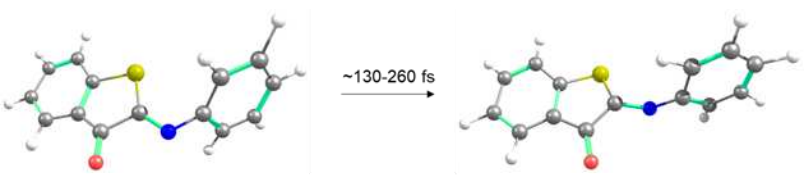
Ideal photochromic systems for biological and medicinal applications are responsive to visible light, show large separation of absorption bands and are functional in water. Recently, a new class of fully-visible-light-operated molecular photoswitches called iminothioindoxyls (ITIs) which meet these requirements was successfully designed [1]. ITIs show an unprecedented band separation of over 100 nm, isomerize on ps time scale and thermally relax on ms time scale. In addition, they exhibit acidochromism [2], which makes them multi-responsive functional systems. By combining advanced spectroscopic techniques and computational methods, we elucidated the photoswitching behavior and acidochromism of ITIs. Using state-of-the-art computational tools, we also addressed the nature of excited states involved in the photoactinic step of the switching process and the dynamics of the photo-excited system from the Franck-Condon region to a conical intersection. This research paves the way towards the development of new photo-controlled systems for a wide variety of applications that require fast responsive functions.



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ACCURATE AB INITIO CALCULATIONS FOR THE ALKALI-METAL AND ALKALINE-EARTH-METAL HYDRIDES

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We report state-of-the-art *ab initio* calculations of the potential energy curves of the $X^1\Sigma^+$ and $A^3\Sigma$ states of the alkali-metal hydrides, and the $X^2\Sigma^+$ and $A^2\Pi$ states of the alkaline-earth-metal hydrides. Adopting the composite approach, the leading term of the interaction energy is calculated involving CCSD(T) method with a Gaussian-type basis sets extrapolated to the complete basis set limit (CBS) on the two-point n^{-3} scheme. We combine it with diagonal Born-Oppenheimer correction and with triples correction emerging from CCSDT calculations performed in basis sets of lower quality. Calculations for the LiH-MgH molecules are performed using DKH method; for the KH-BaH molecules, scalar relativistic effects are included by replacing inner shell electrons in the metal atom with the small-core, fully relativistic pseudopotential. Using the potential energy curves developed by us, we provide theoretical data for the electronic $X^2\Sigma^+ \leftrightarrow A^2\Pi$ transition, characterizing the alkaline-earth-metal hydrides as exquisite candidates for direct laser cooling due to highly diagonal Franck-Condon factors.

EXCITATION AND FRAGMENTATION OF SF_6-REPLACEMENT DIELECTRIC GAS C_3F_7CN: ELECTRONS VS. PHOTONS

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Perfluoroisobutyronitrile C_3F_7CN is a dielectric gas which was developed for the use as an insulation medium in high-voltage circuit breakers. Although SF_6 has been extensively used for this purpose since 1960s, it is an extremely potent greenhouse gas and therefore, efforts are taken to find more environmentally friendly media. C_3F_7CN is one of the most promising candidates, however, its decomposition under the electrical discharge still needs to be fully understood. While the production of charged products has been studied previously [1], the dissociation into neutral fragments poses a much more challenging task. In our work, we addressed this process by combining experimental and theoretical approaches.

First, we studied the primary electronic excitation of the molecule upon interaction with the incident electron beam. We measured the electron energy loss spectra (EELS) at 0° and 180° scattering angles, as well as the UV absorption spectrum, and we contrasted these results with theoretical reference provided by various *ab initio* methods. A strong peak around 10.5 eV corresponding to the $S_0 \rightarrow S_{10}$ transition was observed in both UV spectrum and 0°–EELS, while the $S_0 \rightarrow S_4$ transition around 8.5 eV was suprisingly much more pronounced in the 0°–EELS. The theory is in excellent agreement with these findings. Next, the 180°–EELS experiment indicates that triplet excited states are directly accessible by electron-impact excitation. Finally, we modelled the dissociative pathways in each electronic excited state by means of non-adiabatic molecular dynamics. While the excitation to lower states mainly leads to local minima of excited states, the decay of higher states leads to the formation of either a $–CF_3$ or a –CN fragment.

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DECOMPOSITION OF NORMAL COORDINATES AND HARMONIC VIBRATIONAL FREQUENCIES

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In this work we evaluate and extend a normal mode decomposition scheme first introduced by Boatz and Gordon [1]. With this scheme normal modes are partitioned into their contributions of internal coordinates, i.e., structural parameters like bonds, in-plane/out-of-plane angles and dihedrals. The individual contributions of internal coordinates per normal mode are represented by the diagonal elements of the vibrational density matrices. Furthermore, the scheme assigns to each individual internal coordinate an intrinsic frequency. This intrinsic frequency represents a theoretical frequency value that a vibration would have, if it is solely described by motion of that particular internal coordinate.

We have implemented an almost black box procedure to automatically perform the decomposition for a given Hessian. It will be shown how the normal mode decomposition facilitates normal-coordinate vibrational analysis and the interpretation of normal modes. This is especially the case when normal modes are best described by the coupling of several internal coordinates. The investigated systems will comprise chair-conformational cyclohexane, *cis-cis*-carbonic acid and methanol. Furthermore, state-of-the art notations for the fundamentals of these systems will be examined and evaluated on basis of the decomposition [2, 3, 4].

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Multireference and relativistic DMRG-tailored CC methods.

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In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favorable scaling, it is in practice not suitable for computations of dynamic correlation. We present the DMRG-based tailored coupled cluster (DMRG-TCC) method, which is a "post-DMRG" treatment of dynamic correlation, in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas the dynamic correlation is incorporated through the framework of the CC theory [2, 3].

In order to overcome the single-reference bias of the TCC method, we have developed a Hilbert-space multireference version thereof, which can treat several determinants on an equal footing, and by a multireference analysis of the MPS DMRG wave function get the active amplitudes for each reference. We have assessed this approach on the cyclobutadiene and TME molecules.

We present also the relativistic version of the DMRG-tailored coupled cluster method (4c-DMRG-TCC), aimed at calculations of strongly correlated systems containing heavy atoms. The lower rows transition metal compounds, lanthanides and actinides with open d or f shells combine the complexity of relativistic effects and non-dynamic/dynamic electron correlation and present thus a particular challenge. The 4c-DMRG-TCC method allows to include dynamical correlation at lower computational costs with respect to DMRG in a very large active space, as we demonstrate on the TlH, SbH and AsH molecules [7]. Recently, we developed a general implementation without symmetry restrictions and applied it to study the N-U bond dissociation in the chiral NUHFI molecule.

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BORN APPROXIMATION IN THE CONTEXT OF ELECTRON ENERGY LOSS SPECTROSCOPY

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The energy imparted on a system through electron scattering can be measured through electron energy loss spectroscopy (EELS) with a signal analogous to photoelectron spectroscopy, but with an electron instead of a photon initiating the process. This allows EELS to probe optically forbidden transitions such as singlet-triplet excitations due to relaxed selection rules. The aim of our work is to develop a cheap method for calculating electron impact cross sections which would bypass expensive scattering calculations but would retain sufficient accuracy to represent well the ratios of the cross sections. These will be used as the initial condition for the follow-up calculations of nuclear dynamics.

With this goal in mind, a natural starting point is the Born approximation in which the scattering amplitude can be obtained directly as a matrix element of the potential between the target and the electron represented by a plane wave. This calculation removes the problem of modelling of the continuum making it applicable even to very large systems which are untractable by ab initio scattering codes. However, the method needs to be extended to include exchange interaction in order to treat singlet-triplet transitions. The required integrals have been implemented in the UKRmol+ suite of programs [1] based on the formalism developed by Kuang and Lin [2]. The method is benchmarked by comparing simulated and experimental EEL spectra.

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AB INITIO CALCULATIONS OF ANHARMONIC VIBRATIONAL SPECTRA OF CARBONIC ACID AND CARBONIC ACID METHYL ESTER

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The formation and reactivity of carbonic acid has been subject of interest for over a century. In the late 20th century Hage, Hallbrucker and Mayer [1] studied the formation of carbonic acid and postulated a polymorphism, partially based on infrared spectroscopy studies. This claim remained unchallenged for almost 20 years. However, in their more recent works Bernard [2], and Köck [3] suggested that instead of a polymorphism, the formation of carbonic acid methyl ester takes place. Their works are partially based on the comparison of matrix isolation IR spectra to calculated vibrational spectra, but only within the harmonic approximation. These calculations are reliant on scaling factors to match the experimental data and only show acceptable agreement for wavenumbers below 2000 cm-1. Therefore, the aim of this work is to provide the anharmonic vibrational spectra in order to corroborate their argument. The spectra are calculated with a vibrational configuration interaction (VCI) approach [4] based on a multi-mode potential energy surface (PES) with up to 4-mode couplings using CCSD(T)–F12/VTZ–F12 level of theory for 1- and 2-mode PES terms and CCSD(T)–F12/VDZ–F12 for 3- and 4-mode PES terms. The accuracy of the VCI approach allows for a correct assignment of the bands due to smaller deviation from the experiment than the harmonic approximation and has therefore no need for empirical scaling factors [5].

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STRUCTURE AND SPECTROSCOPIC PROPERTIES OF HYDRATED O_2^- AND O_3^- IONS

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A lot of important chemical reactions occur in solution. Therefore it is of interest, how reactive molecules, like the polyatomic anions superoxide and ozonide, behave in solution. Since the superoxide anion plays a central role in atmospheric chemistry [1] and biochemical processes such as ageing and inflammation [2-3], it is considered to be one of the most important diatomic anions in nature. The ozonide anion plays an important role in the upper atmosphere [1].

We measured the $O_2^-(H_2O)_n$ using Fourier-Transform Ion Cyclotron Resonance Mass Spectroscopy (FT-ICR MS). The spectra show an absorption band at 260-295 nm, with water dissociation as the main channel. We analyse the structures and spectra of hydrated superoxide cluster anions, $O_2^-(H_2O)_n$, $n = 0 - 3$, and hydrated ozonide cluster anions, $O_3^-(H_2O)_n$, $n = 0 - 3$, using density functional calculations. To investigate the lower-energy portions of the potential energy surfaces, several stable structures as well as the geometries of transition states were calculated for each cluster species. We analyse the IR spectra and the UV spectra of the clusters and compare them to experimental data and other computational studies.

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DISSOCIATION PATHWAYS OF HYDRATED MAGNESIUM SULFATE CLUSTERS $[Mg_n(SO_4)_{n-1}(H_2O)_m]^{2+}$

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Hydrated magnesium sulfate clusters are an interesting system both from the application point of view and from the fundamental research point of view. Magnesium sulfate is produced at the boundary between the ocean and the atmosphere. As a sea salt aerosol, it acts as a cloud condensation nucleus, induces rain and might have an important impact on weather and climate. In the form of epsomite it can be used as a long-term thermo-chemical energy storage.

For the fundamental research in physical chemistry, it serves as a model system for understanding complex dissociation pathways in strongly bound clusters. The most important interactions in magnesium sulfate are due to the Coulomb forces between the positively charged magnesium cations and the negatively charged sulfate anions. Due to the strong interactions, different isomers are separated by large energy barriers. Therefore, it is rather difficult for the water molecules to change their location. Also, a reorganization of the entire cluster is energetically very challenging. This plays a key role when modelling the different dissociation pathways.

In order to rationalize the experimentally observed dissociation rates of H_2O and SO_3 by theory, we apply master equation modelling using RRKM theory. For reliable results, a precise description of the different isomers, their energies, the density of states and the reaction pathway is necessary. Due to the complexity of the system this is not trivial and many different approaches have to be tried. For obtaining the different isomers we do not only make use of standard quantum chemical calculations, but also apply genetic algorithms. We use both semi-empirical and density functional theory approaches. We also shed light onto the initial isomer distribution from the electrospray ionization via molecular mechanics simulations. The found isomers are used for multi-well master equation modelling to retrieve rate constants and to obtain insights into how important the isomer distribution is for the total rate constant. The modelling is substantiated through the calculation of electronic excitation spectra.

DFT study of CO_2 activation on $Pd_xPt_{(4-x)}$ clusters in the gas phase

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This study investigates the structure and CO_2-activation reactivity of tetranuclear bimetallic palladium-platinum clusters in the gas phase. Palladium-platinum nanoparticles have been experimentally found to have a low onset potential and high Faradaic efficiency for CO_2 reduction to formic acid [1]. Density Functional Theory studies have also confirmed this alloy's stability against sintering at catalytically relevant temperatures[2]. As such, Pd-Pt clusters are promising candidates for the design of novel catalysts for the CO_2 conversion into fuels. Metal clusters are particularly attractive, as their reactivities can be tuned by their chemical composition and by their size. Thus, different cluster structures and geometries are of particular interest. Our research examines how CO_2 reacts with Pd_xPt_{4-x} clusters using computational methods employing PBE+D3 functional and def2-TZVP level of theory. The geometries of the tetranuclear clusters have been systematically optimized from several possible starting structures and for different spin multiplicities (1,3,5). Structures with the highest atomization energy are selected for further investigation of CO_2 adsorption reactivity. Both dissociated and intact binding modes of CO_2 are analyzed. According to our studies, the tetrahedron-like structure in triplet is the most stable one. We observed that palladium doping of platinum clusters is promoising to tune their reactivity. In particular, we show that the adsorption energy and the activation of CO_2 can be modified systematically by the cluster composition, as shown in Figure 1.

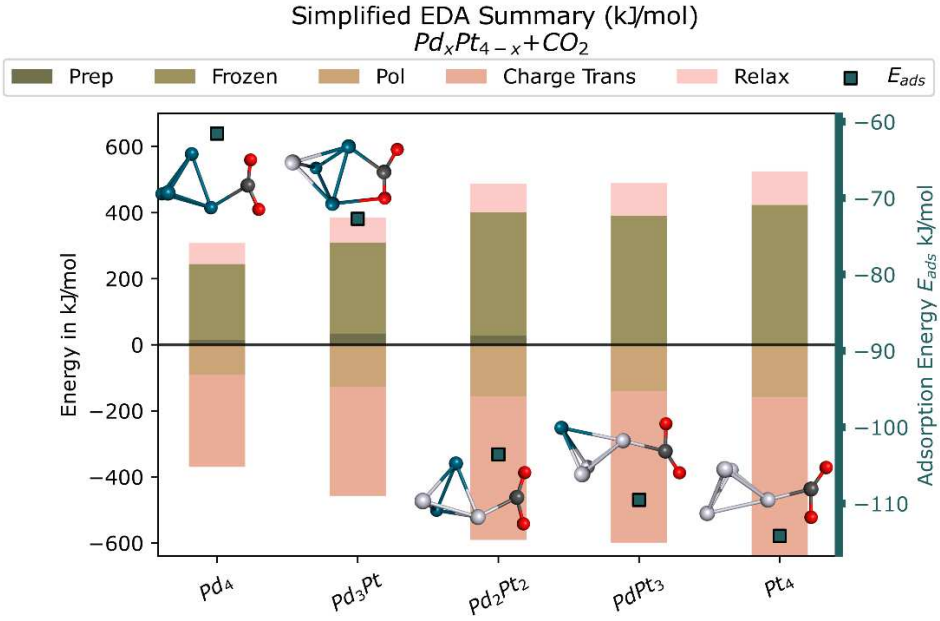

Figure 1: Energy Decomposition Analysis of selected $Pd_xPt_{4-x}+CO_2$ adducts.

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RUNNING HARTREE-FOCK CALCULATIONS IN LOCAL MOLECULAR ORBITALS.

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We have shown an alternative way to obtain the Slater determinant ground state solution within an independent-particle approximation using the exponential ansatz for the wave function (Thouless theorem)[1] and exact treatment in terms of variational coupled cluster singles[2, 3]. The non-terminating expansions of the wave function within the VCCS can be exactly treated by summing up the one-particle density matrix elements in the occupied block using simple recurrence relation. At the same time, this leads to an extremely simple diagonalization-free algorithm for the solution of the Hartree- Fock equations. This treatment corresponds to a non-unitary transformation of orbitals, however, preserving the idempotency of the density matrix. We apply this approach with a starting determinant using localized orbitals, i.e. we present a localized Hartree-Fock method.

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CONFORMATIONAL ANALYSIS OF QUINUCLIDIN-3-ONE DERIVATIVES

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In the self-condensation reaction of quinuclidin-3-one, two distinct isomers are produced in different ratios. To explain this difference in isomer content, full conformational analyses of all 2-(3-hydroxyquinuclidin-3-yl)quinuclidin-3-one stereoisomers were performed. Conformational spaces were calculated by using grid search methods and tensor decomposition of *ab initio* molecular dynamics trajectories. Grid search was performed by rigid scan and a new adaptive relaxed scan method implemented in program *msa*[1] at the semiempirical level of theory using PM7 Hamiltonian. Molecular dynamics simulations were performed using *on-the-fly* calculations of forces in each point of the simulation and velocity Verlet algorithm for integration implemented in program ***qcc***[2]. Principal component analysis was used as a dimensionality reduction tool and performed using a NIPALS algorithm implemented in program ***moonee***[3]. Complete conformational spaces for investigated compounds in the ground state have been determined and results obtained from each individual method have been compared. Use of principal component analysis on generated molecular dynamics trajectories provided the complete set of conformers for every investigated system contrary to the grid search methods, which excluded some of them. Full conformational spaces of enantiomeric pairs were determined with exact match between enantiomeric conformers confirming the validity of used methods and these results are used to explain the differences in self-condensation reaction products.

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Potential inhibitors of SARS-CoV-2 proteases

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The novel zoonotic coronavirus, SARS-CoV-2, remains active and targeted drug development to deactivate the virus replication and cell entry protocol is of great importance. The main protease (M^{pro}) plays crucial role during virus replication and is therefore considered a viable target for potential COVID-19 treatment. Its substrate binding region, consisting of five subsides tolerating different functionalities, is located around Cysteine-Histidine catalytic dyad capable of peptide bond hydrolysis [1,2].

The 3-dimensional structures of 60,407 compounds that join approved drugs, compounds in any phase of clinical trials, substances with human exposure, and compounds tested *in vivo*, were downloaded from the ZINC database [3,4] to serve as potential M^{pro} inhibitors. Semi-flexible docking runs were performed in AutoDock Vina 1.2.2 software [5,6] using AutoDock scoring function. The studied compounds and their poses within M^{pro} cavity were evaluated with respect to compounds' size, free energy of binding (docking score), number of putative hydrogen bonds in formed complexes, etc. Conformational stability of ligand-protein complexes with highest inhibitory potential was validated by methods of molecular dynamics in GROMACS 2018.7 [7-10]. Selected approach reveals several compounds with known side effects that could act as potential M^{pro} inhibitors and represent candidates for future clinical trials.

Parameters describing the affinity of compounds to target protein obtained in this manner were evaluated by artificial intelligence approaches choosing up to 80 % of the *in vivo* set for training and the rest for validation and prediction capability test.

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ASSESSING THE ACCURACY OF QUANTUM MONTE CARLO IN HYDROGEN-BONDED AND STRONGLY CORRELATED SYSTEMS.

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Quantum Monte Carlo (QMC) and its fixed-node approximation (FNDMC) is a promising method of benchmark quality with good trade-off between computational cost and accuracy, which depends however on a trial wave function. Suitability of a single determinant (SD) trial wave function can be evaluated by specific measure of multireference character based on natural orbital occupation numbers [1] reliably obtained at coupled cluster level of theory, which becomes very costly for larger systems. In this work, we show that this diagnostic (δ) can be decomposed by techniques based on many-body expansion and show that two-body fragmentation may lead to a reasonable approximation of such a diagnostic in hydrogen-bonded complexes [2].
In order to asses the reliability of SD FNDMC approach for multireference and strongly correlated systems, we exploit the separation of nondynamic (static and strong) and dynamic correlation and inspect the FNDMC errors relations with static correlation and diagnostics of multireference (MR) character.

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EXPLORING WATER ADSORPTION AND REACTIVITY IN A SERIES OF DOPED ALUMINUM CLUSTER ANIONS

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We present a systematic density functional study of central- and surface-doped aluminum cluster anions $Al_{12}X$ (X = Mg, B, Ga, Si, P, Sc–Zn), their interactions and reactivity with water. Adsorption of water molecules on central-doped clusters is governed by the cluster electron affinity. Doping introduces a dramatic change in the cluster electronic structure by virtue of different ordering and occupation of super-atomic shells, which leads to the creation of complementary active sites controlling the reactivity with water. Surface doping creates unequal charge distribution on the cluster surface, resulting in the adsorption and reactivity of surface-doped clusters being dominated by electrostatic effects. These results demonstrate the strong influence of the doping position on the nature of the interaction and reactivity of the cluster, and contribute to a better understanding of doping effects.

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THEORETICAL DESCRIPTION OF INTERACTING CHROMOPHORES

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The projection based embedding scheme of Hégely et al.[1] was used to describe dual chromophore systems. This density embedding technique allows the formally exact description of ground states intermolecular interaction at DFT level of theory while allowing high level treatment of a subsystem. Benchmark calculations were made for the excited states of solvated chromophores, showing promising results for weakly interacting π-π* excitations. The ground states of dimer systems were investigated to assess the method's ability to describe the potential energy surface. The addition of a dispersion correction gave significant qualitative and quantitative improvement and was included in later calculations. Finally, the excited states a select few dimer systems were calculated with the coupling of the excited states accounted for as the interaction of transition dipoles using the perturbed matrix formalism. The results were promising, albeit in need of further refinement, for π-π* excitation, however π-Rydberg excitations could not even be described qualitatively.

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WHAT CAN WE LEARN BY COMPARING SURFACE HOPPING ALGORITHMS?

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In order to study dynamics of the reactions that involve multiple excited electronic states, it is necessary to use methods beyond the Born-Oppenheimer approximation, i.e. nonadiabatic dynamics methods. Potential energy surfaces of multiple excited states are often complicated because there are many regions where they intersect or become very close in energy so the coupling between nuclear and electronic motion is not negligible. Many different quantum and mixed classical-quantum methods for simulating nonadiabatic processes have been developed.[1] In this presentation the focus is on Landau-Zener surface hopping algorithm which could be very computationally effective since it does not require calculation of nonadiabatic coupling terms. This method is put to the test using well-studied model system and the obtained results are compared with the results given by other nonadiabatic methods.[2, 3]

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MXENE QUANTUM DOTS: EFFECT OF SURFACE/EDGE FUNCTIONALIZATION ON THEIR OPTICAL PROPERTIES

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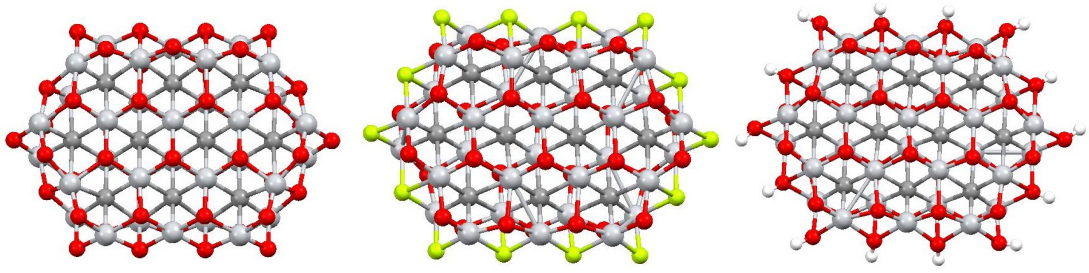
Advances in MXene-derived quantum dots (MXQDs) are in their infancy, but these materials have attracted much interest due to their high electrical conductivity, good biocompatibility, remarkable optical properties and diverse functionalizations [1]. However, a proper understanding of the surface/edge structure is still missing. This study presents possible edge terminations of MXQDs as well as the influence of these functional groups on the optical properties. A 2D Ti_2CO_2 nanosheet was used as a model system to prepare MXQDs consisting of 32 titanium atoms, 10 carbon atoms and 32 oxygen atoms with a different number of surface/edge functional groups. Geometry optimization calculations in different spin states were performed at the density functional theory (DFT) level using the ωB97XD functional along with 6-31G(d,p) basis sets. Absorption spectra were computed within the TD-DFT framework.



(a) $(Ti_2CO_2 - O)$ (b) $(Ti_2CO_2 - F)$ (c) $(Ti_2CO_2 - OH)$

Figure 1: Optimized structure of studied MXQDs with different edge functionalization

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EXCITED STATES OF AURO-CARBONS: CASPT2 and CCSD(T) CALCULATIONS OF C_2Au_2 and C_2Au_4

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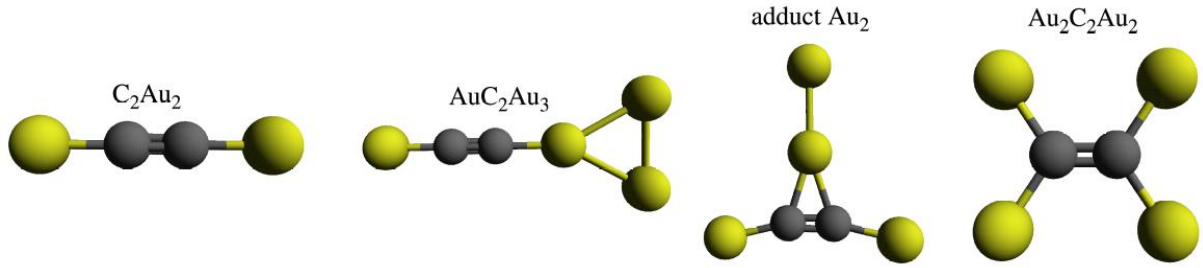
The idea of theoretical calculations of properties of auro-carbons was stimulated by research of P. Pyykkö [1,2] (and other groups) on the analogy between gold and hydrogen in some molecules. However, in contrast to monovalent hydrogen, gold (II) and gold (III) can bind ligands creating e.g. -C-Au-L and other bonds. This allows tuning properties of auro-carbons by selecting a proper ligand. Among properties interesting for applications in opto-electronics belong excited states. In this work we performed pilot calculations on low lying electronic states of the simplest analogs of acetylene and ethylene, i.e. excited states of C_2Au_2 and C_2Au_4 and their conformers. Possible next step is substitution of H by Au atoms in polymers, like in polyethylene [3].

In the first step we have optimized different structures of auro-carbons in the ground state, namely C_2Au_2, $Au_2C_2Au_2$, AuC_2Au_3, and "adduct Au_2" ($AuC\cdots Au_2\cdots CAu$). As a benchmark for next studies, we carefully analyzed the effect of molecule symmetry (C_1 vs. D_{2h} / C_{2v}), basis set size, selection of the active space, and number of averaged states on calculated low lying vertical singlet and triplet excitation energies at the CASSCF and CASPT2 levels. For triplets, the CASPT2 data were compared with CCSD(T) results. We also analyzed the character of frontier orbitals of C_2Au_2, $Au_2C_2Au_2$ molecules as compared with their hydrogen analogs stressing the role of the gold *s*-, *p*-, and *d*- orbitals in auro-carbons. Most importantly, we observe that excitation energies in auro-analogs of acetylene and ethylene are much lower than are excitation energies in their parent hydrocarbons. The major feature of the experimental ethylene spectrum has a maximum at 7.66 eV, but the assignment to the π-π* transition is not generally accepted. The lowest theoretical singlet-singlet transition is around 8 eV, while in $Au_2C_2Au_2$ it is about 2 eV. The character of participating orbitals in C_2H_4 and C_2Au_4 are, of course, totally different.



Ground state structures of considered C_2Au_2 and C_2Au_4 molecules.

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QUANTUM INTERFERENCE EFFECTS IN COLD RB–SR$^+$ COLLISIONS HIGH ABOVE THE ULTRACOLD REGIME

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The *s*-wave scattering regime in ion-atom systems is hard to reach using the currently available experimental techniques. However, in some systems the signatures of *s*-wave scattering can be seen high above the ultracold regime due to the "phase-locking" mechanism, by which the difference between the singlet and triplet scattering phases remains constant over a wide range of partial waves and collision energies. In effect, the *s*-wave scattering modulates the spin-exchange cross sections even at high temperatures. We are building a theoretical model for understanding the collisional properties of the Rb–Sr$^+$ system, investigated experimentally in the group of Prof. Roee Ozeri at the Weizmann Institute of Science. We demonstrate that the phase-locking mechanism plays an important role in determining the spin-exchange cross sections in the Rb–Sr$^+$ system at temperatures much higher than 1 mK. We report the calibration of the $a^3\Sigma^+$ and $A^1\Sigma^+$ molecular potential curves based on the coupled-channel calculations and experimental data, and analyze the prospects for seeing the phase-locking mechanism at work in different ion-atom systems.

EFFECTS OF ELECTRONIC CORRELATION ON THE HIGH HARMONIC GENERATION IN HELIUM

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Attoscience is a rapidly developing area of physics that studies light-matter interactions of atoms and molecules subjected to intense laser fields. One of the key aspects of attoscience is the high harmonic generation (HHG), which provides ultrashort pulses of coherent radiation of wavelength ranging from visible light to soft X-ray. Because of that, HHG has been theoretically studied for decades using a variety of methods. Over the last few years, the real-time propagation of the wavefunction using time-dependent quantum chemical methods coupled to L2-integrable basis sets have gained some recognition in describing the electron dynamics during attosecond processes. Due to a better scaling and much easier handling of multicenter systems, they are slowly surpassing the purely numerical, grid-based approaches.
In our work we investigate the effects of full electronic correlation on the high harmonic generation in the helium atom subjected to laser pulses of extremely high intensity. To do this, we perform real-time propagations of the helium atom wavefunction using quantum chemistry methods coupled to Gaussian basis sets. The calculations are done within the real-time time-dependent configuration interaction framework, at two levels of theory: time-dependent configuration interation with single excitations (TD-CIS, uncorrelated method) and time-dependent full configuration interaction (TD-FCI, fully correlated method). The electronic wavefunction is expanded in Dunning basis sets supplemented with functions adapted to describing highly excited and continuum states. We also compare the TD-CI results with grid-based propagations of the helium atom within the single-active-electron approximation. Our results show that when including the dynamical electron correlation, a noticeable improvement to the description of HHG can be achieved, in terms of e.g. a more constant intensity in the lower energy part of the harmonic plateau [3].

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DFT-based investigation of structure and CO_2 adsorption on zinc dopped copper clusters

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A promising approach to the emission control of carbon dioxide (CO_2) into the atmosphere is the catalytic conversion of this greenhouse gas into valuable compounds. [1] For example, the syngas (mixture of $CO/CO_2/H_2$) has been converted to methanol using heterogeneous copper catalysts. [1,2] Copper, as well as doped copper clusters, have proven to be promising candidates for CO_2 reduction. [3,4] By comparing zinc dopped copper clusters with pure copper clusters, zinc dopped copper clusters show a higher CO_2 reduction activity due to lower activation barriers for CO_2 dissociation. In addition, zinc-doped copper clusters demonstrate easier catalyst regeneration. [4]

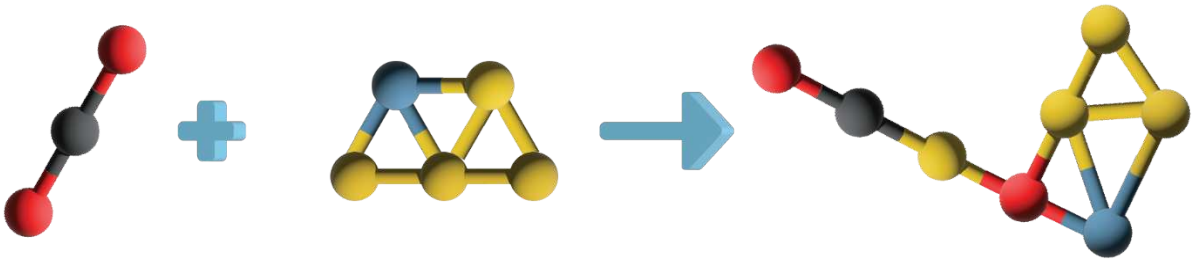

Figure 1: Activation of CO_2 on the Cu_4Zn cluster. Right: Lowest energy structure of the Cu_4Zn-CO_2 adduct in gas phase.

In the present contribution, we have generated a protocol to study these systems using methods based on density functional theory (DFT). We have determined computationally the lowest energy (most stable) structures for the Cu_4Zn cluster as well as the different binding modes of CO_2 on the metal cluster. Calculations for Cu_4Zn revealed that the dissociative adsorption of CO_2 into CO and O is energetically more favorable than non-dissociative adsorption.

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