UNIVERSITY OF WARSAW

New Challenges for Ab Initio Theory in Molecular Science

BOOK OF ABSTRACTS

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01 – 05 July 2025, Warsaw

New Challenges for Ab Initio Theory in Molecular Science
Book of abstracts
01 – 05 July 2025, Warsaw
ncaitms.chem.uw.edu.pl/

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Contents

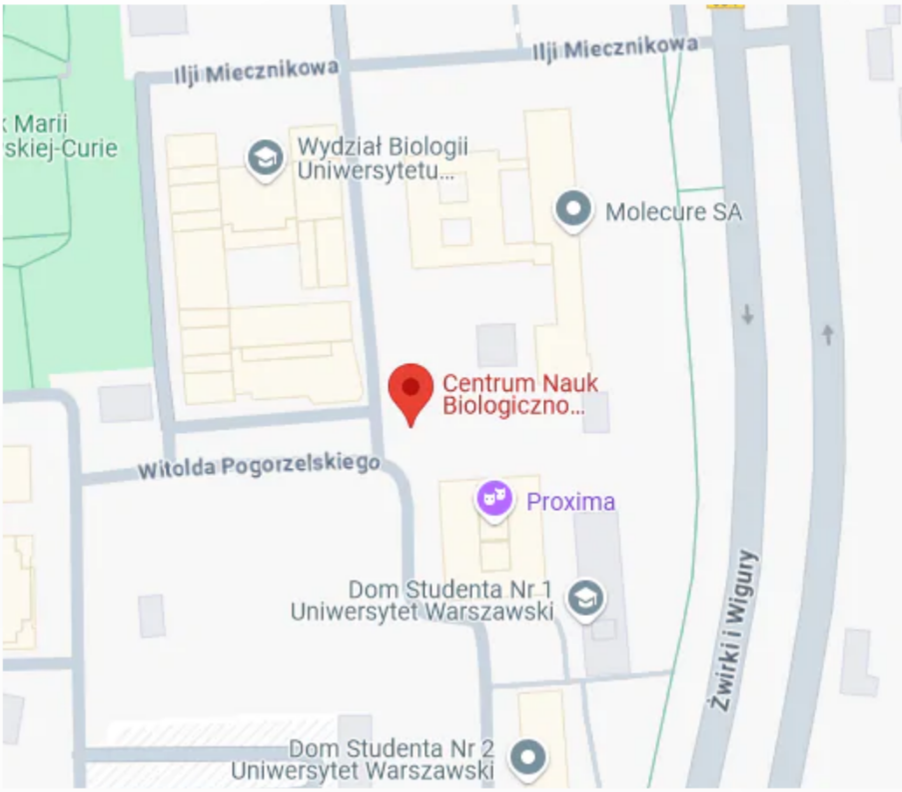
GENERAL INFORMATION

New Challenges for Ab Initio Theory in Molecular Science

1 -5 July 2025

The conference is an extended edition of the workshop *“Intermolecular Interactions: New Challenges for Ab Initio Theory”* (with the latest workshop taking place in 2023) and is dedicated to memory of **Bogumił Jeziorski**, who was an organizer of several recent editions of this workshop. The present conference, in addition to the subject of intermolecular interactions, includes topics such as accurate calculations for few-body systems, precision metrology of fluids, and theory of electron correlation.

Conference venue



The conference will be held at:

Aula A+B,
Biological and Chemical
Research Centre
University of Warsaw
Żwirki i Wigury 101
02-089 Warsaw, Poland

Organizing committee

Grzegorz Chałasiński, University of Warsaw, Poland
Berta Fernández Rodríguez, University of Santiago de Compostela, Spain
Michał Lesiuk, University of Warsaw, Poland
Krzysztof Szalewicz, University of Delaware, USA

GENERAL INFORMATION

Bogumił Jeziorski — life and work

Bogumił Jeziorski was born on April 29, 1947, and passed away on September 15, 2023, at the age of 76. He spent his entire career at the Faculty of Chemistry, University of Warsaw, where he earned his MSc in 1969, PhD in 1975, and DSc in 1982. He was appointed full professor in 1991. Throughout his career, he held visiting positions at several institutions, including University of Delaware, Radboud University Nijmegen, University of Waterloo, University of Florida, and University of Utah.

Bogumił Jeziorski authored approximately 160 scientific publications spanning a broad spectrum of topics in physics and chemistry. His exceptional breadth of knowledge, coupled with a rare talent for generating original scientific ideas, led to fundamental contributions across several research domains. Among his most influential achievements was the development of symmetry-adapted perturbation theory (SAPT), including a practical framework applicable to arbitrary molecular systems, now widely used in quantum chemistry. Another major focus of Bogumił's research was coupled cluster (CC) theory. He introduced the state-universal (Hilbert-space) exponential ansatz for the wave operator, enabling accurate treatment of open-shell atoms and molecules. He also made key contributions to explicitly correlated CC methods based on Gaussian geminals. He was equally engaged in high-precision ab initio calculations for small atoms and molecules. His work included studies of exotic systems with muons, molecular effects in the beta decay of tritium, and interaction-induced properties of helium gas. Notably, the latter contributed to the 2019 redefinition of the International System of Units (SI). Bogumił received numerous honors for his scientific contributions, including the medal of the International Academy of Quantum Molecular Science (1987) and the Prize of the Foundation for Polish Science (2000), the most prestigious scientific award in Poland. He deeply valued collaboration - remarkably, only one of his publications is single-authored. He mentored a large group of PhD students, many of whom now hold faculty positions at leading academic institutions.

Bogumił will be remembered as an exceptional scientist - curious, active, and productive until the very end - and, just as importantly, as an extraordinary human being.

GENERAL INFORMATION

New Challenges for Ab Initio Theory in Molecular Science

Invited speakers

- **Ad van der Avoird**, Radboud University, Nijmegen, Netherlands
- **Zlatko Bačić**, New York University, New York, USA
- **Rodney Bartlett**, University of Florida, USA
- **Małgorzata Biczysko,** University of Wrocław, Poland
- **Tucker Carrington Jr**., Queen's University, Kingston, Ontario, Canada
- **Attila G. Császár**, Eötvös Loránd University, Budapest, Hungary
- **Piotr Froelich**, Uppsala University, Sweden
- **Martin Head-Gordon**, University of California, Berkeley, USA
- **Teresa Head-Gordon**, University of California, Berkeley, USA
- **Gerrit C. Groenenboom**, Radboud University, Nijmegen, Netherlands
- **Trygve Helgaker**, University of Oslo, Norway
- **Piotr Jankowski**, Nicolaus Copernicus University, Toruń, Poland
- **Georg Jansen**, University of Duisburg-Essen, Germany
- **Kenneth Jordan**, University of Pittsburgh, USA
- **Tatiana Korona**, University of Warsaw, Poland
- **Nancy Makri**, University of Illinois at Urbana-Champaign, USA
- **Edit Mátyus**, Eötvös Loránd University, Budapest, Hungary
- **Alston J. Misquitta**, Queen Mary University of London, United Kingdom
- **Monika Musiał**, University of Silesia, Katowice, Poland
- **Hiroshi Nakatsuji**, Kyoto University, Japan
- **Jozef Noga**, Comenius University, Bratislava, Slovakia
- **Marcel Nooijen**, University of Waterloo, Canada
- **Konrad Patkowski**, Auburn University, USA
- **Krzysztof Pachucki**, University of Warsaw, Warsaw, Poland
- **Jiří Pittner**, Academy of Sciences of the Czech Republic, Prague, Czechia
- **Rafał Podeszwa**, University of Silesia, Katowice, Poland
- **Michał Przybytek**, University of Warsaw, Poland
- **Joachim Sauer**, Humboldt University, Berlin, Germany
- **Lyudmila Slipchenko**, Purdue University, West Lafayette, USA
- **Alexandre Tkatchenko**, University of Luxembourg, Luxembourg
- **Michał Tomza**, University of Warsaw, Warsaw, Poland
- **Piotr Wcisło**, Nicolaus Copernicus University, Toruń, Poland
- **Hans-Joachim Werner**, University of Stuttgart, Germany
- **Weitao Yang**, Duke University, Durham, USA
- **Dominika Zgid**, University of Michigan, USA
- **Piotr Żuchowski**, Nicolaus Copernicus University, Toruń, Poland

GENERAL INFORMATION

New Challenges for Ab Initio Theory in Molecular Science

Topics

- Fundamentals of intermolecular interactions
- New developments of density functional theory (DFT) and its applications in theory of intermolecular interactions
- Theory of electron correlation including coupled cluster methods and post-DFT approaches
- Methods applying explicitly-correlated basis sets
- Ultra-high accuracy methods for few-body systems
- Intermolecular interaction in ultra-cold physics and chemistry
- Nonreactive nuclear dynamics of van der Waals clusters
- Open-shell van der Waals clusters
- Applications to systems with dozens or hundreds of atoms
- Applications to soft condensed matter

Extra information for participants

The book of abstracts can be found under the following link:
ncaitms.chem.uw.edu.pl/wp-content/uploads/sites/236/2025/06/book-of-abstracts.pdf
Abstracts are ordered alphabetically.

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Wi-fi password: CNBC_ZwirkiWigury_101

Wi-fi (Aula): AULA_C
Wi-fi password: aula_c_2016

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UNIVERSITY OF WARSAW

Funded by the European Union

GENERAL INFORMATION

New Challenges for Ab Initio Theory in Molecular Science

Types and lengths of the presentations

1) Invited talk: 40 min (35 min talk + 5 min for discussion);
2) Contributed talk: 20 min (17-18 min talk + 2-3 min for discussion);
3) Poster presentation (two poster sessions: Wed, 2 July and Thu, 3 July);

Guidelines for oral presentations

1) Please upload a copy of your presentation to the local computer **at least one session in advance**. You can provide us your slides on a USB drive or (preferably) by sending them via mail to: p.michalak13@uw.edu.pl. Before your session you will be able to check if your slides display correctly. Unfortunately, due to a large number of talks you cannot use your own computer to project slides.
2) Speakers will use the on-ear microphone available in the conference room. Handheld microphones will be used by the chairs and technical support only.
3) The computer in the conference room has the following software installed: Microsoft Powerpoint, Adobe Reader DC, Apple Keynote. However, we strongly encourage all speakers to prepare their final slides in PDF format.
4) The recommended aspect ratio for the slides is 16:9. Please let us know in advance if your slides have a different aspect ratio.

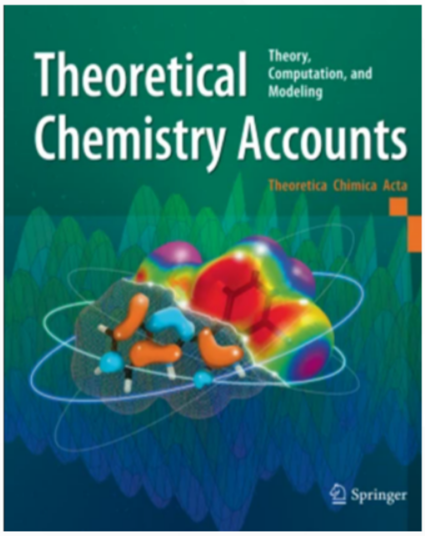
Guidelines for poster presentations

1) The poster stands available at the conference are able to support posters of size A0. Any smaller size will obviously work as well.
2) If your poster presentation is in the first session (Wed, 2 July) you can put up your poster at the very beginning of the conference. However, you have to take it down by morning Thu, 3 July at the latest. If your presentation is in the second session (Thu, 3 July) you can put up your poster in the afternoon and it can stay there until the end of the conference.
3) The organizers will provide equipment needed to put posters on the stands.

GENERAL INFORMATION

New Challenges for Ab Initio Theory in Molecular Science

Special Issue Announcement



We are pleased to announce a special issue of *Theoretical Chemistry Accounts* organized in memory of **Bogumił Jeziorski**. All participants of the conference, including those with oral or poster presentations, are invited to submit research papers to this special issue. The conference organizers will serve as Guest Editors and will be joined by Associate Editor Piotr Piecuch, who will represent the journal as Lead Editor for this issue.

Submissions covering all topics within the scope of *Theoretical Chemistry Accounts* are welcome; however, the editors are particularly interested in contributions related to the research interests of **Bogumił Jeziorski**, including:

- fundamentals of intermolecular interactions;
- new developments in density functional theory (DFT) and its applications to intermolecular interactions;
- theory of electron correlation, including coupled-cluster methods and post-DFT approaches;
- methods employing explicitly correlated basis sets;
- ultra-high accuracy approaches for few-body systems;
- intermolecular interactions in ultracold physics and chemistry;
- nonreactive nuclear dynamics of van der Waals clusters;
- open-shell van der Waals clusters;
- applications of molecular electronic structure methods to systems containing dozens or hundreds of atoms, as well as to soft condensed matter.

As with all submissions to *Theoretical Chemistry Accounts*, manuscripts submitted to this special issue will undergo a peer-review process to ensure the highest quality of accepted papers.

Time	Tue 1 July	Wed 2 July	Thu 3 July	Fri 4 July	Sat 5 July
08:45	Opening				
09:00	I Rodney Bartlett	III Lyudmila Slipchenko	VI Hans-Joachim Werner	IX Martin Head-Gordon	XI Tucker Carrington Jr.
09:40	Monika Musiał	Teresa Head-Gordon	Michał Przybytek	Alexandre Tkatchenko	Ad van der Avoird
10:20	Marcel Nooijen	Tatiana Korona	Edit Mátyus	Rafał Podeszwa	Piotr Jankowski
11:00	**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**
11:30	Trygve Helgaker	IV Weitao Yang	VII Nancy Makri	X Hiroshi Nakatsuji	Piotr Wcisło
12:10	Jiří Pittner	Dominika Zgid	Joachim Sauer	Krzysztof Pachucki	Michał Tomza
12:50	Jozef Noga	* Krzysztof Szalewicz	Małgorzata Biczysko	Piotr Froelich	Lunch break
13:30	Lunch break	Lunch break	Lunch break	Lunch break	
14:30	II Kenneth Jordan	V Graduate students talks	VIII Graduate students talks		XII Zlatko Bačić
15:10	Konrad Patkowski				Attila G. Császár
15:50	Georg Jansen	Poster session I (16:10-18:10)	Poster session II (15:50-17:50)		Gerrit Groenenboom
16:30	**Coffe Break**				Closing
17:00	Piotr S. Żuchowski				
17:40	Alston J. Misquitta				
18:00					
18:20					
19:30		Conference banquet Centre of New Technologies Stefana Banacha 2c			
20:00					

Topics of thematic sessions and lectures:

I	**Coupled cluster theory**
II	**Intermolecular interactions (part 1)**
III	**Intermolecular interactions (part 2)**
IV	**DFT and beyond**
*	**Bogumił Jeziorski - life and work**
VI	**Explicity-correlated methods**
VII	**Soft condensed phase**
IX	**Dispersion in density functional theory**
X	**Ultra-high accuracy calculations**
XI	**Quantum nuclear dynamics (part 1)**
XII	**Quantum nuclear dynamics (part 2)**

Aula A+B, Biological and Chemical Research Center, University of Warsaw
Żwirki i WIgury 101, 02-089 Warsaw, Poland

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Tuesday 01.07.2025

08:45 - 09:00	**Opening**

Session I: Coupled cluster theory

Chairperson
I. Grabowski

09:00 - 09:40	**Rodney J. Bartlett** Correlated Orbital Theory: An Alternative and Complement to Kohn-Sham DFT
09:40 - 10:20	**Monika Musiał** The Coupled Cluster Method Applied to the Study of Open-Shell Systems Based on the Closed-shell Reference Function
10:20 - 11:00	**Marcel Nooijen** Configurational Coupled Cluster

Coffee Break

11:30 - 12:10	**Trygve Helgaker** Variational reformulation of molecular properties in electronic-structure theory
12:10 - 12:50	**Jiří Pittner** Coupled Cluster Methods Externally Corrected by DMRG
12:50 - 13:30	**Jozef Noga** Hartree-Fock via Variational Coupled Cluster Singles with Natural Virtual Orbitals

Lunch Break

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Tuesday 01.07.2025

Session II: Intermolecular interactions, part 1

Chairperson
B. Lesyng

14:30 - 15:10 **Kenneth D. Jordan**
Importance of Charge-Flow Polarization in Polyaromatic Hydrocarbons: Extrapolation to the Image Potential of Graphene

15:10 - 15:50 **Konrad Patkowski**
Decomposing Noncovalent Intramolecular Interactions

15:50 - 16:30 **Georg Jansen**
Revamping the Formalism of Intermolecular Perturbation Theory

Coffee Break

17:00 - 17:40 **Piotr S. Żuchowski**
Response Theory and Molecular Interactions

17:40 - 18:20 **Alston J. Misquitta**
Symmetry-adapted Relaxation Theory (SART): a SAPT-Inspired Theory with Infinite-order Induction Relaxation of Monomers

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Wednesday 02.07.2025

Session III: Intermolecular interactions, part 2

Chairperson
B.Fernández

09:00 - 09:40

Lyudmila V. Slipchenko

Modeling Noncovalent Interactions with
the Effective Fragment Potential Method

09:40 - 10:20

Teresa Head-Gordon

Advances in Force Fields for Molecular Simulation
and Foundation Models

10:20 - 11:00

Tatiana Korona

Symmetry-adapted Perturbation Theory with Monomers Described
on the Coupled Cluster Theory level – theory, challenges, and applications

Coffee Break

Session IV: DFT and beyond

Chairperson
M. Hapka

11:30 - 12:10

Weitao Yang

DFT: Advances in Functional Approximations
and in Theory for Excited States

12:10 - 12:50

Dominika Zgid

Homotopy Continuation Method for
Solving Dyson Equation Fully Self-Consistently

12:50 - 13:30

Krzysztof Szalewicz

Remembering Bogumił Jeziorski and his breakthrough
insights in theory of electron correlation and of intermolecular forces

Lunch Break

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Wednesday 02.07.2025

Contributed talks I

Chairperson
G. Chałasiński

14:30 - 14:45 **Marlene Bosquez Fuentes**

Rovibrational Quantum Dynamics of Simple
Van der Waals Complexes

14:45 - 15:00 **Nikhila Ambika Chandran**

Complete Insensitivity to *Ab Initio* Data: A New Perspective on Modeling
Collision-Induced Absorption of Noble Gas Atoms

15:00 - 15:15 **Humahuti Dihingia**

Towards Accurate Description of Intermolecular Induction

15:15 - 15:30 **Anderson Exlonk Gil Peláez**

Quantum-Informed Machine Learning for Predicting
Fluorescence Quantum Yield

15:30 - 15:45 **Katarzyna M. Krupka**

Single- and Multi-Reference Approaches for Open-Shell
Metal Cluster–PAH Interactions. UMP2C and RS2CC Methods

PROGRAM

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Wednesday 02.07.2025

Poster session I

16:00-18:00

P1	**Iulia Emilia Brumboiu** Computational RIXS: Benchmark and Applications to Organic Molecules Used in Photovoltaics	**P9**	**Marta Gałyńska** A Domain-Based Charge-Transfer Analysis of the First Excited State Calculated with EOM-PCCD+S
P2	**Koushik Chatterjee** Long-range Dispersion Interaction Between Atoms and Molecules in Electronically Excited States	**P10**	**Piotr Gniewek** Interactions of Atomic Ions with Diatomic Molecules
P3	**Dominik Cieśliński** First-Order Symmetry-Adapted Perturbation Theory with Double Exchange for Multireference Systems	**P11**	**Marcin Gronowski** The Electronic Structure of ALF Molecule
P4	**József Csóka** Advancing Quantum Embedding Methods for Modeling Catalytic Environments: Local Approximations and Forces	**P12**	**Tarun Gupta** Induction Energy for Molecules in Excited State - a Comparison of Induction Energy from Finite-Field and SAPT
P5	**Janusz Cukras** Theoretical Prediction of Magneto-Chiral Dichroism for Helicenes and Other Chiral Organic Molecules	**P13**	**Mikolaj Gurba** Effects of Base Stacking on Excitd States in Nucleobase
P6	**Dawid Dąbrowski** The Excited Electronic States of the Helium Dimer Including Adiabatic and Relativistic Effects	**P14**	**Michał Hapka** Correcting Basis Set Incompleteness in Wave Function Correlation Energy by Dressing Electronic Hamiltonian with an Effective Short-Range Interaction
P7	**Achintya Kumar Dutta** A New Perturbative Triples Correction Scheme to Unitary Coupled Cluster Method	**P15**	**Gaurav Harsha** Describing Disorder and Correlation – Coherent Potential Approximation with Bloch Gaussians
P8	**Reinhold Fink** Molecular Orbital Pair Contributions to the Exchange Repulsion Energy Explain the Conundrum of π-Interactions	**P16**	**Hamza Hendaoui** Insights into Rotational (De-)excitation of Interstellar Calcium Dicarbide (c-CaC$_2$) induced by Helium Collisions

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Wednesday 02.07.2025

Poster session I

16:00-18:00

P17	**James Hooper** “A Decomposition of Interaction Energies in Periodic Models and its Insights into Bonding and Descriptors ”	**P23**	**Tymon Kilich** Ultracold Highly Polar KAG and CSAG Molecules: Electronic Structure and Optical Formation
P18	**Munavvar Husain** “Exploring Excited Molecular States via Localized Orbital Locator: A Quantum Topology Analysis of Charge Transfer in the Ethylene–Tetrafluoroethylene Complex”	**P24**	**Adrianna Kruk** Predicting Molecular Excitations induced by a High-Velocity Massive Charged Particle
P19	**Benjamin Adebanjo Ikuesan** “Selected Excited-State Rovibrational and Electronic Structures of the Carbon Monoxide Molecule (Preliminary Result)”	**P25**	**Deepak Kumar** Self-Consistent-Field Solution for Unstable Anions
P20	**Joanna Jankowska** “Molecular-Dynamics Assisted Modeling of Fluorescence Decay in MR-TADF Emitters”	**P26**	**Marta Łabuda** Theoretical Investigations on Fragmentation of Dihydropyran Molecule(C5H8O)
P21	**Dorota Rutkowska-Żbik** DFT Studies on Cu Single Atom and Sub-Nanometer Copper Clusters Deposited on TiO_2 for H_2 Generation	**P27**	**Hela Ladjimi** Radioactive $RaAg^+$ Molecular Ion: Electronic Structure, Formation Schemes, and Prospects for Precision Measurements
P22	**Almaz Khabibrakhmanov** Noncovalent Interactions in Density Functional Theory: All the Charge Density we do not see	**P28**	**Jakub Lang** Third Virial Coefficients of Helium Gas

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Thursday 03.07.2025

Session VI: Explicity-correlated methods

Chairperson
M. Lesiuk

09:00 - 09:40

Hans-Joachim Werner
Accurate Calculations of Non-Covalent Interactions
Using PNO-LCCSD(T)-F12

09:40 - 10:20

Michał Przybytek
Weak Orthogonality Formulation of the Coupled Cluster
Theory with Explicitly Correlated Slater Functions

10:20 - 11:00

Edit Mátyus
The ABC of Triplet Helium Dimer

Coffee Break

Session VII: Soft condensed phase

Chairperson
W. Skomorowski

11:30 - 12:10

Nancy Makri
Small Matrix and Modular Path Integral Methods
for Quantum Dynamics

12:10 - 12:50

Joachim Sauer
Ab Initio Free Energy Simulations with Chemical Accuracy
– Water in Nanoporous Materials

12:50 - 13:30

Małgorzata Biczysko
Validation of Clustering for Quantum-Based Refinement
of Biomacromolecules

Lunch Break

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Thursday 03.07.2025

Contributed talks II

Chairperson
R. Fink

14:30 - 14:45

Rony Letona

Automatic Temperature-Dependent Lattice Free
Energies of Disordered Molecular Crystals

14:45 - 15:00

Omar Rodríguez

Cutting-Edge Machine Learning Approaches for Efficient
and Accurate Reaction Network Analysis

15:00 - 15:15

Edoardo Vanich

Symmetry-Adapted Relaxation Theory (SART):
First-Quantization Hartree-Fock Theory and Implementation

15:15 - 15:30

Bruno von Bruening

New Approach for Distributed Multipole Assessment:
Why You Should use LISA?

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Thursday 03.07.2025

Poster session II

15:50-17:50

P29	**Judith Leson** Long-Range Intermolecular Interactions Involving Excited States of Benzene	**P37**	**Kamil Nalikowski** Embedded Cluster Approach to Describe the Electronic Structure of Doped Crystals
P30	**Bogdan Lesyng** Is the Development of Quantum Modeling Methods Subject to the Laws of Evolution?	**P38**	**Fedor Naumkin** Non- and Reactive Structural Evolution of Intermolecular Systems
P31	**Dibyendu Mahato** Green's Function Integrals with Spherical Gaussian and Plane-Wave-Modulated Basis Functions	**P39**	**Grzegorz Niedzielski** Computational Studies of Molecular Crystal Excited States Using Periodic DFT+U Calculations
P32	**Bartosz Majewski** Theoretical Investigations on Fragmentation of Dihydropyran Molecule(C5H8O)	**P40**	**Jan Okoński** Accurate Ab initio Calculations of Interaction Potentials of the Alkali and Alkaline-Earth Metal Hydrides
P33	**Bilel Mehnen** Rotational Excitation and De-Excitation of the Interstellar Propargyl (H_2CCCH^+) Cation by Collisions with Helium Atoms	**P41**	**Khanh Ngoc Pham** Accuracy of Approximate Methods for Describing Many-Body Contributions of Binding Energies of Molecular Crystals
P34	**Piotr Michalak** Rank-Reduced Equation-of-Motion Coupled Cluster Methods with Triple Excitations	**P42**	**Florian Pimpel** Rank-reduced coupled cluster theory for energy gradients
P35	**Masato Morita** Ab initio Calculations of Feshbach Resonances in Ultracold Collisions Between Rb and AlF	**P43**	**Saikat Roy** Resonance Widths of Autoionizing Rydberg States via Projections Technique Combined with EOM-CCSD Method
P36	**Tymoteusz Mrozek** Accurate Dynamic Polarizabilities in Excited States by Means of ECG Basis Functions	**P44**	**Igor Sawicki** Improving Double Hybrid Functionals via Regularized Second-Order Perturbation Theory

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Thursday 03.07.2025

Poster session II 15:50-17:50

P45	**Jonathan Scherlitzki** Ultrafast Electronic Chirality Flips in the Triatomic Molecule NSF: a New Application of *Ab Initio* Quantum Chemistry	**P52**	**Bartosz Tyrcha** Recent Developments in Second-Quantization-Based Symmetry-Adapted Perturbation Theory
P46	**Leonid Shirkov** Application of SAPT for Constructing Transferable Intermolecular Potentials	**P53**	**Munkhorgil Wang** Comparing Fully Self-Consistency GW (scGW) and Fully Self-Consistency Vertex-Corrected GW (scGWΓ) with Tensor Hypercontraction
P47	**Aditi Singh** Universally Applicable Range-Separation Tuning	**P54**	**Dahvyd Wing** Approximating Pauli Exchange-Repulsion: a Transferable Model Based on Electron Density
P58	**Monika Srebro-Hooper** Exploring Non-Covalent Interactions in Supermolecular Systems Using Density Functional Theory	**P55**	**Henryk Witek** Progress In Exact Analytical Solution of Schrödinger Equation of the Helium Atom
P49	**Korutla Srikanth** Complex Potential Energy Surfaces for Penning Ionization Through Complex Basis Functions	**P56**	**Mateusz Witkowski** Ultrafast Correlation-Energy Estimator
P50	**Krystyna Syty** Multi-level Coupled Cluster Description of Crystal Lattice Energies	**P57**	**Emil Żak** Sharpening Tools for Drug Discovery: Size-Consistent Brillouin–Wigner Second-Order Perturbation Theory Calculations for Molecular Docking and Quantum Algorithms for Modeling Accurate Electronic-Vibrational-Rotational Dynamics
P51	**Aleksandra Tucholska** Enhanced DMRG-AC Approach for Efficient Treatment of Strongly Correlated Systems		

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Friday 04.07.2025

Session IX: Dispersion in density functional theory

Chairperson
M. Pecul-Kudelska

09:00 - 09:40

Martin Head-Gordon
Some Recent Advances in Density Functional Theory:
Three Short Stories

09:40 - 10:20

Alexandre Tkatchenko
Quantum Drude Oscillators for Accurate Modeling of non-Covalent
Interactions in Molecules and Condensed Matter

10:20 - 11:00

Rafał Podeszwa
Dispersionless density functional with physically
correct dispersion correction

Coffee Break

Session X: Ultra-high accuracy calculations

Chairperson
A. Kaczmarek-Kędziera

11:30 - 12:10

Hiroshi Nakatsuji
Exact Scaled Schrödinger Equation Theory Combined with
SAC/SAC-CI Theory and Electrostatic Force Theory

12:10 - 12:50

Krzysztof Pachucki
QED Theory of $X^1\Sigma^+_g$ Energy Levels of H_2

12:50 - 13:30

Piotr Froelich
Rearrangement Collisions of anti-Hydrogen Atoms and Ions with Positronium,
of Interest for Experiments on Fundamental Physics at CERN

Lunch Break

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Saturday 05.07.2025

Session XI: Quantum nuclear dynamics, part 1

Chairperson
B. Braams

09:00 - 09:40

Tucker Carrington Jr.

Exceptionally Accurate ro-Vibrational Energy Levels and Tunnelling Splittings of Water Dimer

09:40 - 10:20

Ad van der Avoird

Para-Ortho H_2 Conversion by Collisions with O_2 and NO

10:20 - 11:00

Piotr Jankowski

How Important are Monomer-Flexibility Effects for Spectra of Van der Waals Clusters?

Coffee Break

11:30 - 12:10

Piotr Wcisło

Towards trapping cold hydrogen molecules

12:10 - 12:50

Michał Tomza

Quantum Control of Ultracold Atom-Ion and Atom-Molecule Collisions

Lunch Break

PROGRAM

New Challenges for Ab Initio Theory in Molecular Science

Saturday 05.07.2025

Session XII: Quantum nuclear dynamics, part 2

Chairperson
M. Biczysko

14:30 - 15:10
Zlatko Bačić
Water Trimer: Rigorous Twelve-Dimensional Quantum Calculations of Intermolecular Vibration-Tunneling States and Low-Frequency Absorption Spectrum

15:10 - 15:50
Attila G. Császár
Quasistructural Molecules

15:50 - 16:30
Gerrit Groenenboom
Rotation-Vibration Inelastic Collision Rates

Closing

UNIVERSITY OF WARSAW

NEW CHALLENGES FOR AB INITIO THEORY IN MOLECULAR SCIENCE

INVITED TALKS

IT-1: WATER TRIMER: RIGOROUS TWELVE-DIMENSIONAL QUANTUM CALCULATIONS OF INTERMOLECULAR VIBRATION-TUNNELING STATES AND LOW-FREQUENCY ABSORPTION SPECTRUM

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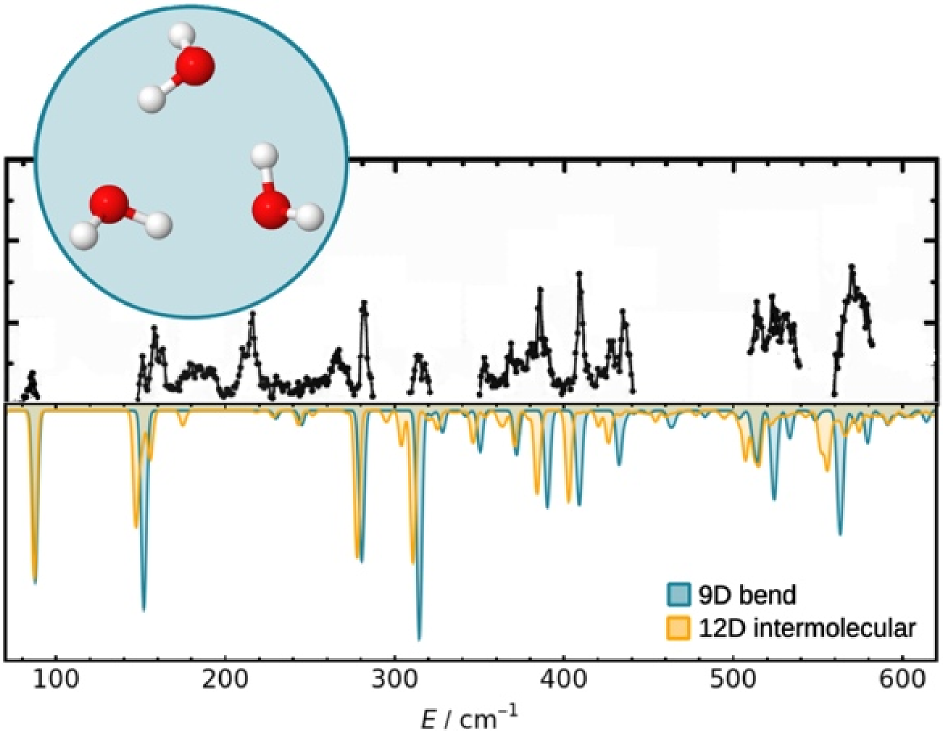
Water trimer is of fundamental importance as the smallest water cluster in which the nonadditive three-body interactions arise. They play a key role in shaping the structural, dynamical, and spectroscopic properties of liquid and solid phases of water and aqueous solutions. The trimer has 12 coupled large-amplitude intermolecular vibrational degrees of freedom (DOFs), and 9 intramolecular DOFs. The complexity of their quantum dynamics is greatly increased by the presence of two low- barrier tunneling pathways, which give rise to elaborate patterns of tunneling splittings. I will present our newly developed methodology which for the first time allows rigorous 12D quantum calculations of the coupled intermolecular vibration-tunneling states of $(H_2O)_3$, with the monomers treated as rigid [1]. The absorption spectrum of the low-frequency vibrations of water trimer simulated using these 12D eigenstates agrees remarkably well with the experimental far-infrared spectrum of the trimer in helium nanodroplets measured by Havenith, Bowman, and co-workers [2], over the entire frequency range of the measurements from 70 to 620 cm^{-1}, as evident from the figure. Moreover, the calculated 12D ground-state torsional tunneling splittings are in excellent agreement with the spectroscopic data. The peaks in the 12D spectrum are often split by the intermolecular stretch-bend Fermi resonances.



[1] I. Simkó, P.M. Felker, and Z.Bačić, J. Chem. Phys., 162 (2025), 034301.

[2] R. Schwan, C. Qu, D. Mani, N. Pal, G. Schwaab, J. M. Bowman, G, Tschumper, and M. Havenith, Angew. Chem., Int. Ed., 59 (2020), 11399.

IT-2: CORRELATED ORBITAL THEORY: AN ALTERNATIVE AND COMPLEMENT TO KOHN-SHAM DFT

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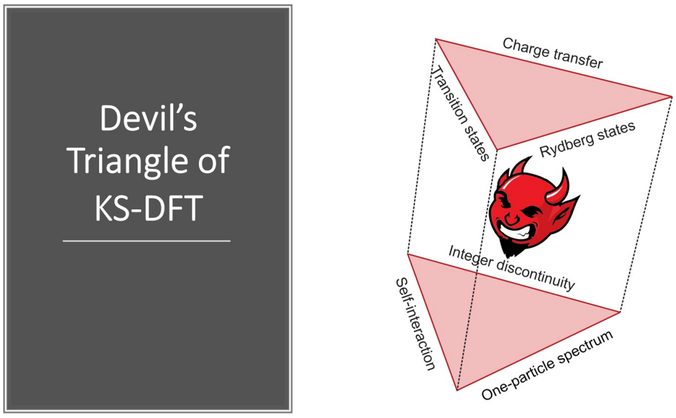
Organic semiconductors are promising materials for next-generation electronics, offering tunable optoelectronic properties. Understanding their electronic excitations is crucial for optimizing performance in applications like photovoltaics and transistors. Density Functional Theory (DFT) provides valuable insights but is computationally expensive for large-scale materials discovery. Machine learning (ML) accelerates this process by predicting electronic properties with high accuracy at a fraction of the cost. ML models trained on DFT data enable rapid screening of candidate materials, uncovering novel organic semiconductors with desirable properties. This synergy between DFT and ML enhances efficiency in materials discovery, paving the way for advanced electronic devices.



Keywords: photoelectron and electronic spectra, coupled-cluster theory, IP/EA-EOM-CC, KS-DFT, response properties

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IT-3: VALIDATION OF CLUSTERING FOR QUANTUM-BASED REFINEMENT OF BIOMACROMOLECULES

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Quantum refinement (Q|R) of crystallographic or cryo-EM-derived structures of biomolecules within the Q|R project aims at using quantum chemical (QM) computations instead of library-based chemical restraints. Advantage of using QM is to describe equally well typical structural properties for standard protein molecules as well as unusual local arrangements of residues in the Ramachandran space, novel ligands, or non-covalent interactions such as π stacking, halogen, hydrogen or salt bridges.

The methods we are developing in the Q|R project [1, 2, 3, 4, 5], an open-source software package (http://github.com/qrefine), combine experimental data with chemical restraints derived from QM (Fig. 1) shown to significantly improve model geometry, in particular the hydrogen bonding. However, extension of the Q|R procedures to very large proteins still poses challenges with relation to tackling the size of macromolecules. One of solutions to this problem adopted in Q|R is development of the automatic divide-and-conquer procedure and validation tools such as an atomic gradient error score that can be easily examined with common molecular visualization programs [5].

Figure 1: Q|R: blend of expertise and software tools.

[1] M. Zheng, J. R. Reimers, M. P. Waller, P. V. Afonine, Acta Cryst. D 73. (2017). 45.

[2] M. Zheng, N. W. Moriarty, Y. Xu, J. R. Reimers, P. V. Afonine, M. P. Waller, Acta Cryst. D 73. (2017). 1020.

[3] M. Zheng, M. Biczysko, Y. Xu, N. W. Moriarty, H. Kruse, A. Urzhumtsev, M. P. Waller, P. V. Afonine, Acta Cryst. D 76. (2020). 41.

[4] L. Wang, H. Kruse, O. V. Sobolev, N. W. Moriarty, M. P. Waller, P. V. Afonine, M. Biczysko, Acta Cryst. D 76 (2020). 1184.

[5] Y. Wang, H. Kruse, N. W. Moriarty, M. P. Waller, P. V. Afonine, M. Biczysko, Theor. Chem. Acc. 142, 100 (2023).

IT-4: EXCEPTIONALLY ACCURATE RO-VIBRATIONAL ENERGY LEVELS AND TUNNELLING SPLITTINGS OF WATER DIMER

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We have used (contracted) basis functions that incorporate coupling between inter-molecular coordinates and coupling between intra-molecular coordinates and an iterative eigensolver to compute many energy levels of water dimer (a 12-D problem). The water monomers are completely flexible. We solve the full problem in a basis of products of intra-molecular and inter-molecular functions. Intra-molecular coordinates specify the shape of the monomers and inter-molecular coordinates specify the relative orientation of the two monomers and distance between them. We are able, for the first time, to compute many monomer-excited states water dimer. To solve the intra-molecular and inter-molecular problems we use the Lanczos algorithm, exploiting the product structure of the primitive basis. We calculate the potential matrix for the full problem without storing the potential on a full-dimensional grid. This is done by storing an intermediate matrix, called the F matrix and parallelizing the calculation. We use a new super accurate potential energy surface computed by S. Yang and D. Zhang, who fit a two-body interaction term with a large number of high-level ab initio points. Agreement with experimental spectra is extremely good. For $(H_2O)_2$ the best experiments probe the inter-molecular levels and the root means square error (RMSE) with respect to experimental levels is 0.29 cm^{-1}; for $(D_2O)_2$ the best experiments probe the intra-molecular levels and the RMSE with respect to 22 of 24 intra-molecular $(D_2O)_2$ levels is 0.17 cm^{-1}. The accuracy of our calculation makes it possible to re-assign several experimental bands.

IT-5: QUASISTRUCTURAL MOLECULES

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While it has become straightforward to understand the structure, spectroscopy, and nuclear dynamics of semirigid molecules, and many quantum chemical models have been developed for them, there are molecular systems for which standard theories of quantum chemistry, like the rigid rotor approximation for the rotational motion and the harmonic oscillator approximation for vibrations, do not provide a sufficient description. These systems include molecules with large-amplitude motion, and especially fluxional and quasistructural molecules. For quasistructural molecules (a) the notion of a static equilibrium structure, corresponding to a minimum on the potential energy surface of the molecule, loses its strict meaning, (b) internal nuclear motions (rotations and vibrations) become dominant, resulting in an effective molecular structure often even qualitatively different from the equilibrium one, (c) separation of the internal nuclear motions breaks down, rotational and vibrational degrees of freedom cannot be separated from each other when interpreting even the lowest rovibrational eigenstates of the molecule, often resulting in effective rotational constants drastically different from the equilibrium ones even for the ground vibrational eigenstate, (d) classification of the rovibrational states requires the use of permutation-inversion symmetry and molecular-symmetry groups, and (e) some of the rovibrational eigenenergies assigned to vibrational parent state exhibit unconventional rotational contributions [1]. Molecules showing quasistructural behavior include neutral species, such as dimethyl acetylene, molecular complexes held together by halogen bonds, and van der Waals complexes (in this lecture the emphasis will be on the nitrogen dimer [2]), as well as charged species, such as H_5^+ [3] and CH_5^+ [4]. It is also of interest to note that in the case of CH_5^+ the rovibrational energy level structure can be understood by a simple, analytically solvable quantum-graph model [5].

[1] A. G. Császár, C. Fábri, J. Sarka, WIREs Comput. Mol. Sci.,10 (2020) e1432.

[2] R. Tóbiás, C. Fábri, M. Bosquez Fuentes, M. Kodrycka, K. Patkowski, and A. G. Császár, Small Struct. (2025) to be submitted.

[3] J. Sarka, C. Fábri, T. Szidarovszky, A. G. Császár, Z. Lin, and A. B. McCoy, Mol. Phys. 113 (2015) 1873.

[4] C. Fábri, M. Quack, and A. G. Császár, J. Chem. Phys. 147 (2017) 134101.

[5] J. I. Rawlinson, C. Fábri, and A. G. Császár, Chem. Comm. 57 (2021) 4827.

IT-6: REARRANGEMENT COLLISIONS OF ANTI-HYDROGEN ATOMS AND IONS WITH POSITRONIUM, OF INTEREST FOR EXPERIMENTS ON FUNDAMENTAL PHYSICS AT CERN

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We present the 4-body calculations of cross sections for collisions of antihydrogen atoms $\bar{\mathrm{H}}$ with positronium $\mathrm{Ps}(n = 1, 2, 3)$, resulting in antihydrogen ions $\bar{\mathrm{H}}^+$. We then consider the subsequent collisions of these ions with positronium, resulting in a coulombically stable $\bar{\mathrm{H}}\mathrm{Ps}$ atomcule, a four-body system that possesses both atomic and molecular properties. These reactions are part of the chain of events in experiments at CERN investigating the fundamental laws of physics, such as Charge Parity Time (CPT) - invariance and gravitational interaction of matter and antimatter. The reaction

$$\bar{\mathrm{H}} + \mathrm{Ps} \rightarrow \bar{\mathrm{H}}^+ + \mathrm{e}^- \tag{1}$$

is a 4-body collisional problem that we solve exactly using the technique of Gaussian Expansion Method (GEM) and combine with the coupled rearrangement channels (CRC) method. The reaction

$$\bar{\mathrm{H}}^+ + \mathrm{Ps} \rightarrow \bar{\mathrm{H}}\mathrm{Ps} + \mathrm{e}^+ \tag{2}$$

presents a 5-body problem that we reduce to the 4-body problem and solve exactly using the technique of GEM and CRC. The characteristic feature of our calculations is the simultaneous use of several Jacobi coordinates in expansion of the multichannel wave functions. The scattering matrix S and the cross sections are obtained from the coupled, non-local integro-differential equations that explicitly couple all open channels.

We present the cross sections for rearrangement collisions (1), (2) and for all other processes that compete with the rearrangement outcome. The accuracy of the cross sections is reported in terms of the unitarity of the S matrix. We discuss the near-threshold features of the scattering cross sections and show that they comply with the expected behaviour stipulated by the Wigner's law. We also visualize, via the 3-dimensional probability density plots, the mechanism of the rearrangement reaction (2) whereby $\bar{\mathrm{H}}^+$ shrinks and gets more tightly bound by capturing the electron, while the positron carries away the excess of energy.

In this talk we will also reflect on the broad interests of Bogumil Jeziorski, including quantum chemistry applied to fundamental physics. This entails his contributions to the determination of the upper bounds to the electronic neutrino mass, and studies of fusion reactions in muonic molecules. Collaboration with Bogumil on these, at the time, visionary subjects inspired the author to enter another futuristic area: the interaction of matter and antimatter.

IT-7: ROTATION-VIBRATION INELASTIC COLLISION RATES

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Over 300 molecules have been detected in space, and this number is rapidly increasing. At typical densities of interstellar environments, the populations of quantum states, and hence the intensity of observed spectra, do not follow from the kinetic temperature of the gas. Instead, they depend on absorption and emission of photons and transitions due to collisional processes involving He, H, and H_2. Radiative transfer modeling is required to extract densities and temperatures, from the observations. These models critically depend on accurate molecular input data, particularly on collision rates. The mid-infrared instrument (MIRI) of the James Webb Space Telescope (JWST) is observing rotation-vibration transition for molecules such as CO_2, HCN, C_2H_2, H_2O, HC_3N, and an abundance of other organic molecules, see, e.g., Ref. [1].

I will present results for ro-vibrational collision rates for He+CO_2, where we include the bend and symmetric stretch modes [2, 3]. A five-dimensional potential energy surface is computed at the CCSD(T)-F12/aug-cc-pVTZ level, and we obtain cross sections from coupled channels calculations. In CO_2 there is a Fermi resonance between the symmetric stretch and two quanta in the bend. I'll discuss convergence and other issues encountered when computing rate coefficients for all transitions between the Fermi resonance states and the vibrational ground state, for radiative transfer modeling up to temperatures of 500 K. I'll also discuss successes and failures of approximate methods such as the coupled states, nearest-neighbor coupled states, infinite order sudden, and distorted wave Born approximation.[2, 4] Finally, I'll present preliminary results of radiative transfer modeling using the computed collision rates.

[1] A. M. Arabhavi, I. Kamp, Th Henning, E. F. van Dishoeck, *et al*, Science 384 (2024) 1086.

[2] Taha Selim, Ad van der Avoird, and Gerrit C. Groenenboom, J. Chem. Phys., 159 (2023) 164310, ibid. 157 (2022) 064105.

[3] Taha Selim, Ph. D. thesis (Radboud University Nijmegen, 2024.

[4] Taha Selim, Arthur Christianen, Ad van der Avoird, and Gerrit C. Groenenboom, J. Chem. Phys., 155, 034105 (2021).

IT-8: SOME RECENT ADVANCES IN DENSITY FUNCTIONAL THEORY:THREE SHORT STORIES

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Density functionals are inexact in by design because that presents the possibility of achiev- ing high efficiency and acceptable accuracy. Assessments of accuracy therefore play a crucial role in practical density functional theory. In this talk I will discuss topics related to this general issue. The first is presenting a new database that we call the ”Gold Standard Chemical Database 138” (GSCDB138), which is a substantial expansion and revision of the earlier ”Main Group Chemical Database 84” (MGCDB84). In addition to revisions for accuracy, GSCDB138 includes a range of new chemically relevant energy differences that characterize the density, indirectly assess excited states, and directly probe key molecular properties. It also expands coverage of the periodic table to include an extensive range of energy differences in transition metal containing compounds. GSCDB138 assessments of leading density functionals will be reported [1]. Next, preliminary progress on the design of a new functional using this database will be discussed [2]. Thirdly, I will discuss identifying and correcting issues associated with the smoothness of the widely used Grimme D3 and D4 dispersion corrections [3, 4].

[1] J. Liang and M. Head-Gordon (work in progress).
[2] J. Liang and M. Head-Gordon (work in progress).
[3] N.V. Tkachenko and M. Head-Gordon, J. Chem. Theory Comput. 20 (2024), 9741.
[4] N.V. Tkachenko, L.B. Dittmer and M. Head-Gordon, J. Phys. Chem. Lett. 15 (2024), 10629.

IT-9: ADVANCES IN FORCE FIELDS FOR MOLECULAR SIMULATION AND FOUNDATION MODELS

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I will discuss a number of methodological advances using crude force fields for foundation models in chemistry, accurate many-body force fields under non-reactive approximations, as well as force fields for reactivity. These will be illustrated applications in hydrogen combustion and microdroplet chemistry.

IT-10: VARIATIONAL REFORMULATION OF MOLECULAR PROPERTIES IN ELECTRONIC-STRUCTURE THEORY

Trygve Helgaker[1], *Poul Jørgensen*[2], *Jeppe Olsen*[2], *Magnus Bukhave Johansen*[3], *Theo Juncker von Buchwald*[3,4], *Andreas Erbs Hillers-Bendtsen*[3], *Kurt V. Mikkelsen*[3]

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Conventional quantum-mechanical calculations of molecular properties, such as dipole moments and electronic excitation energies, give errors that depend linearly on the error in the wave function. An exception is the electronic energy, whose error depends quadratically on the error in wave function. We here describe how all properties may be calculated with a quadratic error, by setting up a variational Lagrangian for the property of interest [1, 2] Because the construction of the Lagrangian is less expensive than the calculation of the wave function, this approach substantially improves the accuracy of quantum-chemical calculations without increasing cost. As illustrated for excitation energies, this approach enables the accurate calculation of molecular properties for larger systems, with a shorter time-to-solution and in a manner well suited for modern computer architectures.

[1] P. Jørgensen, J. Olsen, M. B. Johansen, T. J. von Buchwald, A. E. Hillers-Bendtsen, K. V. Mikkelsen, and T. Helgaker, “A variational reformulation of molecular properties in electronic-structure theory”, Sci. Adv., 10 (2024), eadn3454 (1024).

[2] A. E. Hillers-Bendtsen, M. B. Johansen, T. J. von Buchwald, K. V. Mikkelsen, J. Olsen, P. Jørgensen, and T. Helgaker, “Cluster perturbation theory. XI. Excitation-energy series using a variational excitation-energy function”, J. Chem. Phys. 162, 024114 (2025).

IT-11: HOW IMPORTANT ARE MONOMER-FLEXIBILITY EFFECTS FOR SPECTRA OF VAN DER WAALS CLUSTERS?

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A global full-dimensional description of interactions in a molecular van der Waals cluster, including both inter and intramolecular degrees of freedom, may seem to be the necessary starting point for high-accuracy nuclear dynamics calculations. Such calculations are currently able to predict properties of clusters accurately enough to be confronted with experiment [1, 2] However, the all-dimensional treatment becomes prohibitively expensive already for clusters with more than 6 atoms due to the dimensionality "curse". On the other hand, the rigid-monomer approximation allows applications to much larger clusters. We show that if the rigidity is imposed via averaging over monomer vibrations [3, 4], the predictions from such a reduced-dimensionality model can be about as accurate as those from the full-dimensional one. This is shown on the example H_2–CO, for which measured extensive rovibrational spectra provide a stringent evaluation of theoretical results. The averaging of the interaction energy surface V may be approximated by applying Taylor expansion of V with respect to intramolecular coordinates. Such a procedure leads to the rovibrational spectra without any noticeable loss of accuracy. Consequently, there is no need to develop the full-dimensional interaction energy surface, which implies further savings.

[1] X.-G. Wang, T. Carrington, Jr., Chem. Phys. 148 (2018), 074108.

[2] M. Stachowiak, E. Grabowska, X.-G. Wang, T. Carrington, Jr., K. Szalewicz, P. Jankowski, Sci. Adv. 10 (2024), eadj8632.

[3] M. Jeziorska, P. Jankowski, K. Szalewicz, B. Jeziorski, J. Chem. Phys. 113 (2000), 2957.

[4] P. Jankowski, J. Chem. Phys. 121 (2004), 1655.

IT-12: REVAMPING THE FORMALISM OF INTERMOLECULAR PERTURBATION THEORY

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Starting from the Dirac picture of quantum mechanics it is shown that the common long- range polarization approximation variant of intermolecular perturbation theory can be reformulated through connected correlation functions. This naturally leads to a representation of the interaction energy contributions as integrals over monomer properties. It also yields an alternative to compute the dispersion energy which hitherto seems not to have been explored. Furthermore, a simplified derivation of the short-range exchange- overlap contributions appearing in second-order symmetry-adapted perturbation theory (SAPT) will be presented which also paves the way to eliminate the standard overlap approximation in higher orders of SAPT.

IT-13: IMPORTANCE OF CHARGE-FLOW POLARIZATION IN POLYAROMATIC HYDROCARBONS: EXTRAPOLATION TO THE IMAGE POTENTIAL OF GRAPHENE

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In this talk the role of charge-flow polarization along a sequence of increasingly large $C_{6n}{}^{2}H_{6n}$ (n=1,2,3,...) polyaromatic hydrocarbons (PAHs) is explored. It is demonstrated that a charge-flow polarization model parameterized to reproduce calculated ab initio polarizabilities of small PAHs when applied to very large (60,000 C atoms) gives a polarization potential close to the 1/4|z| classical image potential expected for graphene. The resulting polarization model is incorporated in a model Hamiltonian and used to characterize the non-valence anion states of a series of PAHs. It is demonstrated that in the $n \to \infty$ limit, the electron binding energies approach those of the image potential states of graphene. These results demonstrate the connection between the non-valence anion states of small molecular systems and the image potential states of nanoscale graphitic materials.

IT-14: SYMMETRY-ADAPTED PERTURBATION THEORY WITH MONOMERS DESCRIBED ON THE COUPLED CLUSTER THEORY LEVEL – THEORY, CHALLENGES, AND APPLICATIONS

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Accurate determination of intermolecular interaction energy within symmetry-adapted perturbation theory (SAPT) would be impossible without a adequate treatment of electron correlation within monomers. In more than 40 years of the SAPT development, many approaches have been proposed for this purpose. Since coupled cluster (CC) theory is one from the most popular electronic structure theories, it was natural to make an attempt to apply it within SAPT. However, a proper formulation of SAPT(CC) is quite nontrivial because the CC theory is nonvariational and e.g. does not fulfill the Hellmann-Feynman theorem. In this talk, some intricacies of this formulation will be discussed and explained, especially those related to the definition of two-electron density matrices. Additionally, complications occuring with a practical implementation will be addressed, which are related to a high scaling of the calculations of frequency-dependent density susceptibilities, and the way of reducing this cost by the application of density-fitting technique will be presented. Finally, example applications of SAPT(CC) will be presented.

IT-15: SMALL MATRIX AND MODULAR PATH INTEGRAL METHODS FOR QUANTUM DYNAMICS

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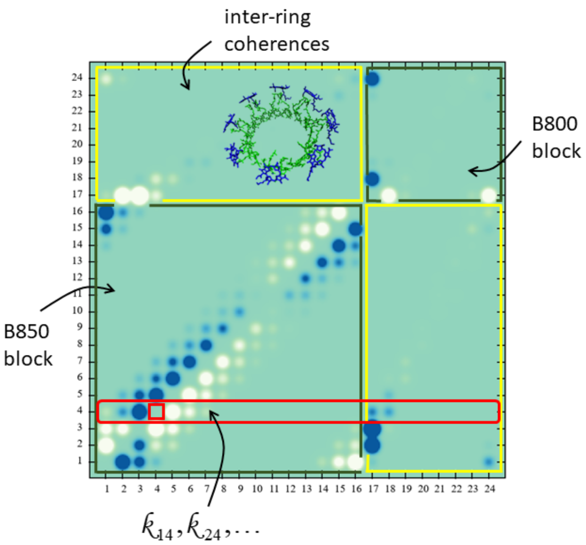
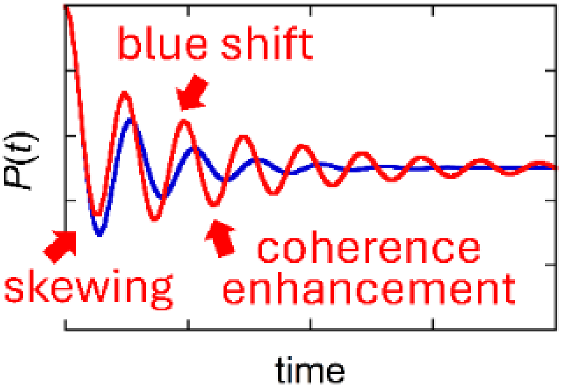
Since the early 1990s, the iterative, tensor-based quasi-adiabatic propagator path integral (QuAPI) methodology has enabled numerically exact, fully quantum mechanical simulations of system-bath dynamics. Recent work showed that one can further disentangle the path integral variables through the rigorous small matrix decomposition (SMatPI), which leads to expressions that involve a discrete convolution and thus have the structure of the generalized quantum master equation (GQME), with matrices of size equal to that of the system's reduced density matrix (RDM). By eliminating tensor storage, the SMatPI algorithm enables the simulation of multistate systems and long-memory processes. A modular decomposition of the path integral (MPI) allows calculations in systems of many interacting system-bath units with effort that scales linearly with the number of units. Besides generating the populations and coherences of electronic states over a range of temperatures, the path integral simulations track the evolution of electronic-vibrational densities, revealing the impact of individual and collective vibrational modes on charge and energy transfer, and have identified quantum mechanical signatures of regular and chaotic motion as well as intriguing topological phase effects. By grouping paths into equivalence classes, the path integral methods can be implemented for a large number of system Hamiltonians without additional cost, allowing the inclusion of time-dependent fields and static disorder. Further, the rich information content of the time-evolving RDM can be efficiently conveyed through coherence maps, which offer a powerful visualization tool for understanding the creation and destruction of quantum superpositions and enable a state-to-state pathway analysis of dynamical processes. Recent work has extended these ideas to Hamiltonians that involve anharmonic baths, utilizing propagation matrices constructed by parsing the influence functional from the system's environment. These methods allow the exploration of novel effects induced by essential bath anharmonicity, which cannot be captured by effective harmonic bath mappings.





IT-16: THE ABC OF TRIPLET HELIUM DIMER

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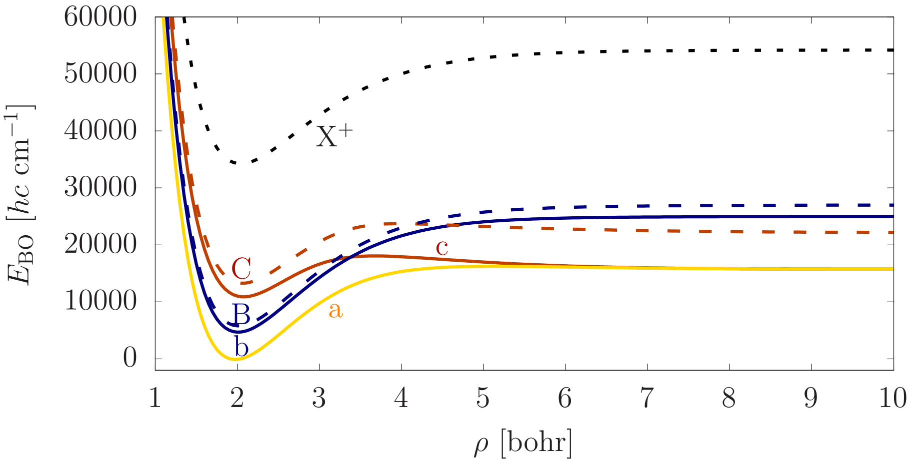
The ground electronic state of the helium dimer, He$_2$ $\mathrm{X}\ ^1\Sigma_\mathrm{g}^+$, has been extensively studied by Jeziorski and co-workers. It is very weakly bound by dispersion forces and its potential energy curve supports a single vibrational state. This work focuses on the electronically excited states of the helium dimer, which possess a highly complex rovibronic energy level structure with intriguing magnetic properties, recently attracting experimental interest in generating cold molecules and precision physics. We computed the potential energy curves (PEC) of the a $^3\Sigma_\mathrm{u}^+$, b $^3\Pi_\mathrm{g}$, and c $^3\Sigma_\mathrm{g}^+$ electronic states, converged to a few ppm $(1:10^6)$ precision using variationally optimised floating explicitly correlated Gaussian functions (fECGs). The Born-Oppenheimer (BO) PECs were appended with diagonal BO, regularised relativistic, and quantum electrodynamical (QED) corrections. The non-adiabatic coupling, as well as relativistic (spin-spin, spin-orbit) couplings, appended with QED corrections for the anomalous magnetic moment of the electron, were also computed with the fECG wave functions. Furthermore, we have included (a less accurate) representation of the B $^1\Pi_\mathrm{g}$ and C $^1\Sigma_\mathrm{g}^+$ electronic states for the relativistic couplings with the b and c states. Non-adiabatic vibrational and rotational mass corrections were computed for modelling non-adiabatic effects due to distant electronic states. The coupled rovibrational and rovibronic equations are solved using the discrete variable representation. The X$^+$ $^2\Sigma_\mathrm{g}^+$ ground state of the He$_2^+$ cation and all bound rovibrational energies with relativistic, QED, and non-adiabatic corrections are also recomputed resulting in an estimated few ppb $(1:10^9)$ accuracy. All in all, the ionisation, electronic, vibrational, rotational, and fine-structure splitting energy intervals of the lowest-energy triplet helium dimer states were obtained with unprecedented accuracy, spanning a total of nine orders of magnitude of the energy scale and being accurate to at least five or six digits at all scales of motions. The computed results aim to help guide and interpret ongoing and future experimental work on this simple excimer.



IT-17: SYMMETRY-ADAPTED RELAXATION THEORY (SART): A SAPT-INSPIRED THEORY WITH INFINITE-ORDER INDUCTION RELAXATION OF MONOMERS

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Symmetry-adapted perturbation theory (SAPT), in its many flavours, remains the foundation of much of our understanding of intermolecular interaction energies. This is not only because of the high accuracies of SAPT-like theories (SAPT2, SAPT2+3, SAPT(DFT), SAPT(CCSD), SAPT(MC), etc.), but also because of the physical interpretation of the interaction energy and the well-defined asymptotic expansions for each of the non-exchange terms in SAPT approaches. However, none of the SAPT methods are true perturbation theories as all rely on a post-, non-perturbative correction to account for missing higher-order induction terms (using the so-called 'delta-Hartree–Fock' term $\delta_{\rm int}^{\rm HF}$), and additionally to include induction–dispersion couplings (using the 'delta-MP2' term $\delta_{\rm int}^{\rm MP2}$). Further, because all practical SAPT approaches are based on the weak symmetry forcing of symmetrized-Raleigh–Schrödinger (SRS) perturbation theory, the theories are of use only at low orders in perturbation theory.

Here we propose a new foundation for a SAPT-like formalism that is based on the variational principle, and the non-orthogonal relaxation of monomer wavefunctions in the electrostatic and exchange potentials of the partners. This theory, termed symmetry-adapted relaxation theory (SART), obtains the induction interaction of the monomers to infinite-order in the interaction operator. SART results in physical terms for the monomer deformation energies, the electrostatic, exchange, and induction energies. As the SART approach is variational, it results in a density matrix which can be used to define interaction-induced properties. In our implementation of SART based on Hartree–Fock theory, or SART[HF], the dispersion energy must be included via perturbation theory. Like SAPT, the SART formalism does not contain the BSSE, and obtains the interaction energy of the complex directly. In the case of SART[HF] we obtain the supermolecular Hartree–Fock interaction energy exactly without explicitly computing the supermolecular wavefunction. While SART[HF] is an important proof-of-principle, it forms the foundation of correlated SART methods and SART based on density-functional theory.

IT-18: THE COUPLED CLUSTER METHOD APPLIED TO THE STUDY OF OPEN-SHELL SYSTEMS BASED ON THE CLOSED-SHELL REFERENCE FUNCTION

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Determination of molecular and spectroscopic properties using the coupled cluster (CC) method in open-shell systems is usually carried out on the basis on the UHF or ROHF functions. The disadvantages of this approach are well-known and are manifested either in the difficult convergence of solutions (also at the post-Hartree-Fock level) or in breaking spin symmetry. In recent years, a number of new formulations of the CC method have been developed, related to the theory of equation-of-motion or to the multi-reference approach, allowing the description of open-shell states based on the RHF reference function [1]. Such formulations include methods allowing the description of states formed after the removal (IP) or addition (EA) of an electron to the system, which allow the description of systems containing one unpaired electron. In the case of methods describing states after removal (DIP) or addition (DEA) of two electrons, we have the possibility of describing triplet systems or systems that dissociate homolytically into open-shell fragments. Configurations with two or three excess electrons (sectors (2,0) and (3,0) in Fock space (FS), respectively) have proven to be particularly useful in determining precise potential energy curves associated with dissociation of a single bond for excited states of alkali and alkaline earth metal diatomics. The FS(2,0) method is used where closed shell fragments are formed during dissociation of a dipositive ion and FS(3,0) - a tripositive ion. Example calculations illustrating the usefulness of the FS method in one, two and three valence sectors have been performed, among others, for selected alkali and alkaline earth metal diatomics. In all cases, solutions with the correct symmetry and correct potential energy curves were obtained.

[1] M. Musiał, S. A. Kucharski, Advanced models of coupled-cluster theory for the ground, excited, and ionized states. *Adv. Quantum Chem.: Polish Quantum Chemistry from Kołos to Now*, 87 (2023), 73-113.

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IT-19: EXACT SCALED SCHRÖDINGER EQUATION THEORY COMBINED WITH SAC/SAC-CI THEORY AND ELECTROSTATIC FORCE THEORY

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In natural science, the so-called “God Equation” is important. Newton’s equation of motion is an example. It should be solvable and its exact solutions must give exact predictions of phenomena, like Newton’s equation of classical mechanics. In quantum mechanics, Schrödinger equation, however, had long been insolvable in the exact sense, but in 2004, the exact method of solving this equation has been formulated by this author [1] by proposing scaled Schrödinger equation that is equivalent to the original Schrödinger equation. Exact solutions for small systems have proven the toughness of the theory. Recently, the theory was combined with the SAC/SAC-CI theory [2, 3, 4] and the Hellmann-Feynman electrostatic force theory [5, 6], and applied to larger systems like benzene for ground, excited, and ionized states. In this lecture, the usefulness of our exact theory as a general predictive theory will be shown.

[1] H. Nakatsuji, Phys. Rev. Lett. 93 (2004), 030403; Phys. Rev. A 72 (2005), 062110.

[2] H. Nakatsuji and K. Hirao, J. Chem. Phys. 68 (1978), 2053.

[3] H. Nakatsuji, Chem. Phys. Lett. 59 (1978), 362.

[4] H. Nakatsuji, Acta Chimica Hungarica – Models in Chemistry 129 (1992), 719.

[5] H. Hellmann, “Einfuehrung in die Quantenchemie,’ Deuticke, Leipzig, 1937; R. P. Feynman, Phys. Rev. 56 (1939), 340.

[6] H. Nakatsuji, J. Am. Chem. Soc. 95 (1973), 345, 354; 96 (1974), 24, 30.

IT-20: HARTREE-FOCK VIA VARIATIONAL COUPLED CLUSTER SINGLES WITH NATURAL VIRTUAL ORBITALS

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Fifteen years ago, 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] via variational coupled cluster singles (VCCS) [2, 3] approach. The non-terminating expansions of the wave function within 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.

Recently, we have applied this approach using the VCCS expansion in determinants created from localized orbitals both in the occupied and the virtual subspaces. Such approach gave rise to *a priori* localized Hartree-Fock method [4]. It turned out that the latter approach can be advantageous for rather large systems, only [4]. Here we present first results with calculations using natural virtual orbitals instead of the localized ones. Unlike with localized VCCS now the virtual space can be significantly reduced from the very beginning, which provides a unique algorithm leading to reducing the computation time by orders of magnitude.

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[1] D. J. Thouless, Nucl. Phys. 21 (1966) 225-232.
[2] J. Noga and J. Šimunek, J. Chem. Theory Comput. 6 (2010) 2706-2713.
[3] J. Šimunek and J. Noga, AIP Conf. Proc. 1504 (2012) 143-151.
[4] J. Šimunek and J. Noga, J. Comput. Chem. 46 (2025) e70075.

IT-21: CONFIGURATIONAL COUPLED CLUSTER

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In this presentation we discuss a Configurational Coupled Cluster approach. The systems of interest are described by a chain (or ring) of sites, each with a local Hilbert space of (neutral, many-body) states. The basis states for the complete system are simple tensor products of the states for the subsystem. Prototypical examples are chains of planar or linear rotors, or magnetic Hamiltonians. We currently limit systems to linear chains, usually periodic, that can show interesting quantum phase transitions as a function of a coupling strength. We use an exponential operator excitation operator to describe states of the system, where each component operator only excites on limited sites (single, double, triple, etc.). Our focus will be a description of various realizations of the theory. The simplest theory is a single reference CCC theory. This can be extended to a time-dependent theory, and we extract eigenstate information from the time-dependent wave function. If time permits also a CCC thermofield theory will be discussed that allows the direct calculation of thermal properties. The theory is potentially a step towards the description of strongly correlated systems in electronic structure theory.

IT-22: QED THEORY OF $\mathrm{X}^1\Sigma_g^+$ ENERGY LEVELS OF H$_2$

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We will present Quantum Electrodynamic theory of the molecular hydrogen together with the calculations of energy levels with sub-MHz accuracy [1] using the 4-body explicitly correlated exponential basis functions [2, 3].

[1] K. Pachucki and J. Komasa, in preparation (2025).
[2] K. Pachucki and J. Komasa, JCTC **20**, 8644 (2024).
[3] K. Pachucki and J. Komasa, Phys. Rev. A **109**, 032822 (2024).

IT-23: DECOMPOSING NONCOVALENT INTRAMOLECULAR INTERACTIONS

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Noncovalent interactions between parts of the same molecule are essential for predicting thermodynamic and kinetic stability of isomers, the properties of molecular balances, and the second-sphere effects in catalysis. However, a decomposition of intramolecular interactions into physical terms, such as those in symmetry-adapted perturbation theory (SAPT), presents a challenge due to a lack of an unambiguous definition of interacting subsystems. To initiate a perturbation series, one needs to come up with a noninteracting description of two nonbonded fragments **A** and **B** covalently connected by a linker **C**. In the most "SAPT-like" ISAPT approach [1], this is done by computing Hartree-Fock wavefunctions for **A** and **B** embedded in the Fock matrix of **C**. However, standard ISAPT suffers from unphysical energy terms, such as repulsive hydrogen-bond electrostatics, due to artificial dipole moments at the **A-C** and **B-C** boundaries. We recently proposed a redistribution of the interfragment bond electrons to reduce those dipoles [2]. The resulting ISAPT variant leads to physically reasonable energy decomposition for all fragmentation patterns, and it was used to investigate nonbonded interactions in hydrocarbons, pentanediol isomers, molecular balances, [2] and substituted cis- and trans-azobenzenes [3]. While ISAPT is now able to provide a physical interpretation of the nonbonded interaction between fragments **A** and **B** in the presence of **C**, it cannot quantify the *entire* nonbonded interaction within a molecule. As the first step towards the latter goal, we proposed to forgo molecular fragmentation in favor of a range separation of the interaction potential, identifying its long-range part with noncovalent interaction [4]. The neglect of short-range terms still leads to reasonably accurate SAPT and ISAPT corrections, establishing range separation as a hopeful alternative to fragmentation. This approach dates back to the idea of Professor Jeziorski to regularize the attractive singularities in the intermolecular Coulomb potential to make the SAPT expansion convergent [5].

[1] R. M. Parrish, J. F. Gonthier, C. Corminboeuf, and C. D. Sherrill, J. Chem. Phys., 143 (2015), 051103.

[2] D. Luu and K. Patkowski, J. Phys. Chem. A, 127 (2023), 356.

[3] D. Luu and K. Patkowski (to be published).

[4] D. Luu, C. Corminboeuf, and K. Patkowski, J. Chem. Theory Comput., 20 (2024), 7884.

[5] K. Patkowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys., 120 (2004), 6849.

IT-24: COUPLED CLUSTER METHODS EXTERNALLY CORRECTED BY DMRG

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The DMRG-tailored CC (TCC) method is a promising approach for some types of strongly correlated molecules. In order to overcome the single-reference bias of the TCC method, we have developed a Hilbert-space multireference version of tailored CC, which can treat several determinants on an equal footing. We have employed a multireference analysis of the DMRG wave function in the matrix product state form to get the active amplitudes for each reference determinant and their constant contribution to the effective Hamiltonian. We have implemented and compared the performance of three Hilbert-space MRCC variants - the state universal one, and the Brillouin-Wigner and Mukherjee's state specific ones. We have assessed these approaches on the cyclobutadiene and tetramethylenethane (TME) molecules, which are both diradicals with exactly degenerate determinants at a certain geometry.

We have also developed a fully general implementation of the relativistic 4c-DMRG-TCC method, covering complex and quaternion double group symmetry. The 4c-TCC method thus becomes applicable to polyatomic molecules including heavy atoms. For assessment of the method, we performed calculations of the chiral uranium compound NUHFI, which was previously studied in the context of the enhancement of parity violation effects. In particular, we performed calculations of a cut of the potential energy surface of this molecule along the dissociation of the N-U bond, where the system exhibits a strong multireference character.

Orbital entropies, pair entropies, and mutual information have become popular tools for analysis of strongly correlated wave functions. We introduces a spin-free orbital entropy, pair entropy, and mutual information, which simplify the correlation analysis and are invariant with respect to M_s of a spin multiplet. By comparison of these quantities with their "original" spin-including counterparts one can distinguish static correlation due to spin couplings from the "genuine" strong correlation due to a multiconfigurational character of the wave function. We illustrate the approach on a model consisting of a non-interacting dimer of triplet diradicals and on a more realistic example of iron-sulfur bound complexes with one and two iron atoms.

[1] Demel O., Brandejs J., Lang J. Brabec J., Veis L., Legeza Ö., Pittner J., J. Chem. Phys. **159**, 224115 (2023).

[2] Višňák J., Brandejs J., Máté M., Visscher L., Legeza Ö, Pittner J., J. Chem. Theory Comput. **20**, 8862–8875 (2024).

[3] Pittner J., Mol. Phys. (2025) https://doi.org/10.1080/00268976.2025.2500632.

IT-25: DISPERSIONLESS DENSITY FUNCTIONAL WITH PHYSICALLY CORRECT DISPERSION CORRECTION

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Accurate dispersion energies from symmetry-adapted perturbation theory, based on the density functional theory description of the monomers [SAPT(DFT)], enable the development of an atom-atom dispersion formula that effectively models dispersion interactions across a wide range of intermonomer separations. When combined with a dispersionless density functional (dlDF) [1], designed to capture only the non-dispersion components of the interaction energy, the resulting dlDF+D approach provides a physically sound decomposition of the interaction energy. This method remains accurate across a wide range of intermolecular distances, including both the potential energy minimum and the asymptotic region. Accurately capturing both of these regimes has long posed a challenge for standard dispersion-corrected DFT functionals.

Over time, the dlDF+D methodology has been systematically extended and improved, both in its treatment of dispersion [2, 3] and in its underlying DFT framework [4]. These developments and their distinctions will be reviewed in the talk.

[1] K. Pernal, R. Podeszwa, K. Patkowski, and K. Szalewicz, Phys. Rev. Lett., **103**, (2009) 263201.

[2] R. Podeszwa, K. Pernal, K. Patkowski, and K. Szalewicz, J. Phys. Chem. Lett. **1**, 550 (2010).

[3] W. Jedwabny, E. Dyguda-Kazimierowicz, K. Pernal, K. Szalewicz, and K. Patkowski, J. Phys. Chem. A, **125**, 1787 (2021).

[4] A. U. Rehman and K. Szalewicz, J. Chem. Theory Comput., **21**, 1098 (2025).

IT-26: WEAK ORTHOGONALITY FORMULATION OF THE COUPLED CLUSTER THEORY WITH EXPLICITLY CORRELATED SLATER FUNCTIONS

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Until recently, the weak orthogonality functionals were typically combined with the Gaussian-type geminals (GTG) for the expansion of the coupled cluster pair functions [1]. Unfortunately, all GTG-based approaches require costly nonlinear optimizations of a large number of the GTG exponential parameters. For one-center systems an interesting alternative is to use a Hylleraas basis set of explicitly correlated Slater functions,

$$\frac{1}{4\pi}\, r_1^u r_2^v r_{12}^t \, e^{-a_i r_1 - a_j r_2},$$

where $a_i,\, a_j > 0$, and $u,\, v,\, t$ are non-negative integers, for the expansion of the pair functions. This basis set requires introduction of only a handful of nonlinear parameters per electron pair, making their optimization a straightforward task. The Hylleraas basis set has not found a significant use in the coupled cluster theory thus far because of the resulting three-electron integrals. However, in the past few decades considerable progress has been achieved in attempts to evaluate them analytically and/or recursively [2].

The Hylleras basis set can be systematically extended so that the basis set limits and the corresponding errors bars are easier to estimate. This made it possible to compute pair-correlation energies of the beryllium atom with error smaller than $10^{-12}E_\mathrm{h}$—an improvement of several orders of magnitude in comparison with the previous works—effectively removing the basis set incompleteness error in this component of the energy.

[1] B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys., 81 (1984), 368.

[2] K. Pachucki, M. Puchalski, and E. Remiddi, Phys. Rev. A, 70 (2004) 032502.

IT-27: AB INITIO FREE ENERGY SIMULATIONS WITH CHEMICAL ACCURACY – WATER IN NANOPOROUS MATERIALS

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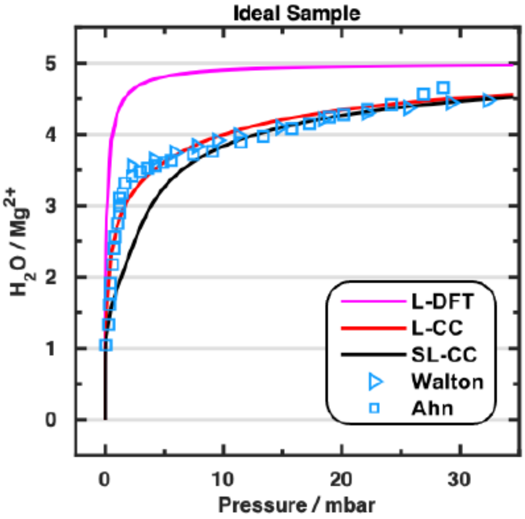
Free energy simulations require (i) a method to calculate the potential energy surface (PES), and (ii) a method to sample the potential energy. The "standard model" of computational catalysis uses (i) DFT with some account of dispersion, and (ii) local sampling using harmonic partition functions. Obtaining chemically accurate (± 4 kJ/mol) results requires going beyond the "standard model" in both respects. We present a general local approach that uses our hybrid QM:QM method [1] to calculate CCSD(T)-quality PESs for stationary points, samples the PES locally with anharmonic partition functions [2], and uses Grand Canonical Monte Carlo lattice simulations for global sampling over the sites [3]. We consider adsorption in nanoporous materials, specifically H_2O and alkanes in H-zeolites [4] and H_2O, CO_2, CH_4, N_2, and CO in metal-organic frameworks (MOFs). MOFs are versatile platforms for various applications including water harvesting and carbon capture and storage. The design of improved MOFs requires the reliable prediction of adsorption isotherms with "chemical" accuracy. While DFT has provided atomistic understanding of the H-bonded structures involved in the water-filling mechanism of MOF-303 [5], chemical accuracy for adsorption energies is rarely achieved with DFT, even if dispersion is taken into account. Here, we employ our hybrid QM:QM approach to get accurate adsorption energies. We use Gibbs free energies from vibrational partition functions ("analytical sampling") as input for predictions of adsorption isotherms based on multi-site or multi-step Langmuir models. Our predicted isotherms are in close agreement with experiments for carefully prepared samples. The figure shows that our approach yields close agreement with experiments (Walton, Ahn, blue symbols) when Coupled Cluster-level QM:QM energies are used for the multi- and stepwise-Langmuir models (L-CC and SL-CC, respectively), whereas DFT (PBE+D3) predicts much too high loadings for a given pressure, and full loading is reached already at much too low pressures. Comparison with other experiments yields agreement only if we assume that part of the adsorption sites are blocked. We conclude that ab initio QM:QM simulations have reached a level of accuracy that deviations between computational predictions and experiments indicate sample imperfections.



[1] J. Sauer, Acc. Chem. Res. 52 (2019), 3502.

[2] G. Piccini, M. Alessio, J. Sauer, Y. Zhi, Y. Liu, R. Kolvenbach, A. Jentys, J. A. Lercher, J. Phys. Chem. C 119 (2015), 6128.

[3] K. Sillar, A. Kundu, J. Sauer, J. Phys. Chem. Lett. 8 (2017), 2713.

[4] F. Berger, M. Rybicki, J. Sauer, ACS Catal. 13 (2023), 2011.

[5] N. Hanikel, X. Pei, S. Chheda, H. Lyu, W. Jeong, J. Sauer, L. Gagliardi, O. M. Yaghi, Science, 374 (2021), 454.

IT-28: MODELING NON-COVALENT INTERACTIONS WITH THE EFFECTIVE FRAGMENT POTENTIAL METHOD

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Non-covalent interactions control the structure, dynamics, and function of molecular assemblies and biological systems. In this talk, we will discuss our recent developments of the Effective Fragment Potential (EFP) method, a general polarizable ab initio-based force field that provides an accurate description of the non-covalent interactions. The EFP pairwise energy decomposition analysis allows the decomposition of non-covalent interactions into contributions from individual components of the molecular system, which facilitates the analysis of structure-function relations in complex assemblies. We will show applications of the EFP and QM/EFP methods for modeling non-covalent interactions in molecular crystals, protein-ligand complexes, and photosynthetic proteins.

IT-29: REMEMBERING BOGUMIŁ JEZIORSKI AND HIS BREAKTHROUGH INSIGHTS IN ELECTRONIC STRUCTURE THEORY

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Scientific community lost a leader in the field of electronic structure theory when Bogumił Jeziorski passed away on 15 IX 2023, at the age of 76. He was active in research almost until his last days. Throughout his professional life, Bogumił was associated with the Faculty of Chemistry of the University of Warsaw, from MSc in 1969, through PhD in 1975, DSc in 1982, to professorship in 1991. Bogumił's deep knowledge of physics, chemistry, and mathematics—in addition to his ability to create new ideas—resulted in breakthrough developments in several fundamental areas of physics and chemistry. He is best known for his work in theory of intermolecular interactions, in particular the development of the symmetry-adapted perturbation theory (SAPT) [1], the explanation of its convergence properties [2], and the development of practical methods applicable to arbitrary molecules [3]. SAPT is currently the mainstream method for calculating intermolecular forces. Another area of Bogumił's research was the coupled cluster method (CC). In particular, he introduced the so-called state-universal (in Hilbert space) exponential form of the wave operator for open-shell atoms and molecules [4]. He also developed the CC method using explicitly correlated Gaussian basis functions [5]. Another field of his activity was high-precision calculations for small atoms and molecules, including studies of exotic molecules containing muons [6]—important for understanding muon-catalyzed nuclear fusion, molecular effects in beta decay of the tritium atom [7]—important for measuring the mass of the neutrino, and properties of the helium atom [8], including the interaction of these atoms [9]. The latter work required the application of relativistic quantum mechanics and quantum electrodynamics. The results of this research were used in 2019 to formulate a new international standard for temperature [10].

[1] B. Jeziorski, R. Moszyński, and K. Szalewicz, Chem. Rev. 94, 1887 (1994).

[2] K. Szalewicz, R. Bukowski, and B. Jeziorski, in Theory and Applications of Computational Chemistry: The First Fourty Years, edited by C. E. Dykstra et al., (Elsevier, 2005) Chap. 33, pp. 919–962.

[3] S. Rybak, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. 95, 6576 (1991).

[4] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A 24, 1668 (1981).

[5] K. Szalewicz and B. Jeziorski, Mol. Phys. 108, 3091 (2010).

[6] K. Szalewicz, B. Jeziorski, A. Scrinzi, X. Zhao, R. Moszy nski, W. Kolos, P. Froelich, H. J. Monkhorst, and A. Velenik, Phys. Rev. A 42, 3768 (1990).

[7] O. Fackler, B. Jeziorski, W. Kołos, H. J. Monkhorst, and K. Szalewicz, Phys. Rev. Lett. 55, 1388 (1985).

[8] K. Piszczatowski, M. Puchalski, J. Komasa, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 114, 173004 (2015).

[9] M. Przybytek, W. Cencek, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 119, 123401 (2017).

[10] G. Garberoglio, C. Gaiser, R. M. Gavioso, A. H. Harvey, R. Hellmann, B. Jeziorski, K. Meier, M. R. Moldover, L. Pitre, K. Szalewicz, and R. Underwood, J. Phys. Chem. Ref. Data 52, 031502 (2023).

IT-30: QUANTUM DRUDE OSCILLATORS FOR ACCURATE MODELING OF NON-COVALENT INTERACTIONS IN MOLECULES AND CONDENSED MATTER

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An accurate description of polarization response and van der Waals interactions in atomistic systems usually requires computationally intensive, hence not widely applicable, high-level quantum-mechanical methods. For realistic systems, more efficient models are needed that should not only be parameterized to enable accurate calculations, but also yield insights into how non-covalent interactions scale in atomistic systems composed of many interacting moieties. Here, I discuss an accurate, efficient, and insightful quantum Drude oscillator (QDO) model, which has been widely used in the description of the electronic response of atoms, molecules, and materials, as well as for the modeling of polarization and van der Waals dispersion interactions in an incredibly wide array of systems. The focus is on showing how the model is able to accurately capture the po- larization response of many-electron atoms and how noncovalent interactions (including exchange repulsion, polarization, and dispersion) emerge for QDO dimers. Furthermore, the QDO model is shown to yield accurate scaling laws that allow one to understand the evolution of polarizability, exchange-repulsion, and dispersion interactions across the periodic table of elements, as well as for molecular systems. By bridging physical insight and computational efficiency, the QDO model offers a powerful and versatile framework for the modeling of noncovalent interactions across inorganic solids, molecular materials, and nanostructured systems.

IT-31: QUANTUM CONTROL OF ULTRACOLD ATOM-ION AND ATOM-MOLECULE COLLISIONS

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Ultracold atoms and molecules are a unique playground for quantum chemistry and quantum physics [1], because the quantum effects and quantum control are amplified at ultralow temperatures. Such systems offer numerous exciting research prospects ranging from quantum-controlled chemical reactions and quantum simulations to precision spectroscopic measurements probing the fundamental laws of nature. I will present our recent results of ab initio electronic structure and multichannel quantum scattering calculations proposing, guiding, and explaining ultracold experiments. I will start with ultracold ion-atom mixtures, where a single ion in a Paul trap is immersed into ultracold atomic gas. Previously, in collaboration with experimental groups in Amsterdam and in Freiburg, we reached and explained the quantum regime of ion-atom collisions manifested via shape resonances [2] and their quantum control with an external magnetic field observed with magnetic Feshbach resonances [3]. We have now discovered that quantum control may be possible at much higher temperatures under specific conditions [4]. I will continue by explaining the mechanism of recently observed magnetic Feshbach resonances in ultracold Na+NaLi atom-molecule mixtures [5]. In collaboration with groups at MIT and in Nijmegen, we showed that these Feshbach resonances result from spin-rotation and spin-spin couplings in combination with the anisotropic atom-molecule interaction. I will conclude by discussing hyperfine-to-rotational energy transfer in ultracold Rb+KRb atom-molecule collisions [6]. In collaboration with groups at Harvard and in Reno, we found that electronic spin is strongly coupled with molecular rotation in this system. If time allows, I will discuss our most recent efforts in proposing new classes of ultracold molecules for probing physics beyond the Standard Model.

[1] T. Karman, M. Tomza, J. Pérez-Ríos, Ultracold Chemistry: a testbed for theoretical few-body physics, Nature Phys. 20, 722 (2024).

[2] T. Feldker, H. Fürst, H. Hirzler, N. V. Ewald, M. Mazzanti, D. Wiater, M. Tomza, R. Gerritsma, Buffer gas cooling of a trapped ion to the quantum regime, Nature Phys. 16, 413 (2020).

[3] P. Weckesser, F. Thielemann, D. Wiater, A. Wojciechowska, L. Karpa, K. Jachymski, M. Tomza, T. Walker, T. Schaetz, Observation of Feshbach resonances between a single ion and ultracold atoms, Nature 600, 429 (2021).

[4] M. Z. Walewski, M. D. Frye, O. Katz, M. Pinkas, R. Ozeri, M. Tomza, Quantum control of ion-atom collisions beyond the ultracold regime, Science Adv. 11, eadr8256 (2025).

[5] J. J. Park, H. Son, Y.-K. Lu, T. Karman, M. Gronowski, M. Tomza, A. O. Jamison, W. Ketterle, Spectrum of Feshbach resonances in NaLi + Na collisions, Phys. Rev. X 13, 031018 (2023).

[6] Y.-X. Liu, L. Zhu, J. Luke, M. C. Babin, M. Gronowski, H. Ladjimi, M. Tomza, J. L. Bohn, T. V. Tscherbul, K.-K. Ni, Hyperfine-to-rotational energy transfer in ultracold atom-molecule collisions of Rb and KRb, Nature Chem. 17, 688 (2025).

IT-32: PARA-ORTHO H_2 CONVERSION BY COLLISIONS WITH O2 AND NO

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It is well known among spectroscopists that two modifications of hydrogen exist: para-H_2 and ortho-H_2. Pure para-H_2 can be prepared by leading a 1:3 para:ortho mixture of “normal” H_2 over a catalyst at low temperature, and can be kept for a long time also at room temperature. More than ninety years ago Farkas and Sachsse [1] measured the rate coefficient of para-ortho H_2 conversion in gas mixtures with the paramagnetic open-shell molecules O_2, NO, and NO_2. In the same year, 1933, it was proposed by Wigner [2] that it is the magnetic dipole-dipole coupling between the electron spin of the paramagnetic molecule and the nuclear spins of the two protons in H_2 that is responsible for the conversion. In asymmetric collisions this coupling makes the two H-nuclei inequivalent and mixes the nuclear spin functions of para- and ortho-H_2, as well as their rotational states with even and odd j values. Another mechanism was proposed later and suggested to be much more effective: the exchange interaction with the open-shell molecule induces spin density into the electronic wavefunction of H_2 and makes the H-nuclei inequivalent by hyperfine interactions through the Fermi contact term.

We theoretically investigated [1] the para-ortho H_2 conversion by collisions with O_2 in a first principles approach. Both mechanisms were taken into account and the corresponding coupling terms were quantitatively evaluated as functions of the geometry of the O_2-H_2 collision complex by means of ab initio electronic structure calculations. Then they were included in nearly exact quantum mechanical close-coupling scattering calculations for the collisions between O_2 and H_2, which yielded the para-ortho H_2 conversion rate coefficients for temperatures up to 400 K. The conversion rate and its temperature dependence are in good agreement with the values measured in H_2-O_2 gas mixtures. The calculations provide detailed insight into the conversion process.

Farkas and Sachsse [3] found, surprisingly, that NO is 3 to 12 times more effective in para-ortho H_2 conversion than O_2. Calculations for NO-H_2 are much more difficult than for O_2-H_2, because NO has two spin-orbit states: $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and the spin is strongly coupled to the NO axis by spin-orbit coupling. Moreover, the $^2\Pi$ state is spatially degenerate, so that non-adiabatic coupling is important. Our most recent theoretical results, which are in quantitative agreement with the measurements, show that the peculiar activity of NO versus O_2 originates from a totally unexpected mechanism.

[1] L. Farkas and H. Sachsse, Z. Phys. Chem. B, 23 (1933) 1.

[2] E. Wigner, Z. Phys. Chem. B, 23 (1933) 28. (2014) 195.

[3] X. Zhang, T. Karman, G.C. Groenenboom, and A. van der Avoird, Nat. Sci., 1 (2021) e10002.

IT-33: TOWARDS TRAPPING COLD HYDROGEN MOLECULES

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Due to its simplicity, H_2 constitutes a perfect tool for testing fundamental physics: testing quantum electrodynamics, determining fundamental constants, or searching for new physics beyond the Standard Model. H_2 has a huge advantage over the other simple calculable systems of having a set of a few hundred ultralong living rovibrational states, which implies the ultimate limit for testing fundamental physics with H_2 at a relative accuracy level of 10-24. The present experiments are far from this limit. I will present our so far results of an ongoing project aimed at trapping cold H_2. We develop an ultra-strong optical dipole trap. The time-dependent potential is going to recapture the coldest fraction of the cryogenic H_2 cloud.

[1] H Jóźwiak, P Wcisło, Scientific Reports 12, 14529 (2022).

[2] H Jóźwiak, TV Tscherbul, P Wcisło, J. Chem. Phys. 160, 094304 (2024).

IT-34: ACCURATE CALCULATION OF NON-COVALENT INTERACTIONS USING PNO-LCCSD(T)-F12

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Non-covalent interactions (NCIs) are fundamental to understanding biomolecular systems, material properties, and chemical reactivity. Accurately modeling these forces requires reliable theoretical benchmarks since experimental data are rarely available. CCSD(T) has long been the “gold standard” reference for computing NCIs. Due to the high cost of CCSD(T), previous NCI benchmarks mainly focus on smaller molecules (typically < 50 atoms). The application of CCSD(T) to larger systems is made possible by applying local coupled-cluster approximations [LCCSD(T)]. This is crucial to address still underexplored challenges such as extended π-conjugated, stacked molecular aggregates (100–300 atoms, e.g. important in opto-electronics), supramolecular assemblies or host-guest systems (50–250 atoms), and protein-ligand complexes (100–400 atoms in the QC region). Recent comparisons of LCCSD(T) and FN-DMC results indicate an overbinding tendency of CCSD(T) in larger π-stacked complexes and other NCI systems with high polarizability [1, 2, 3]. However, the reliability of such comparisons depends crucially on the accuracy of the local approximations in the LCCSD(T) calculations, as well as on remaining basis set incompleteness errors. The explicitly correlated PNO-LCCSD(T)-F12 method in Molpro [4], possibly combined for very large systems with the recently introduced region approach [5], offers solutions to these problems by minimizing both local as well as basis set errors. This method bridges the gap between computational efficiency and high accuracy. Here it is used to reexamine key NCI systems previously evaluated using FN-DMC and other LCCSD(T) methods, and to provide new reliable benchmark results [5].

[1] A. Benali, H. Shin, and O. Heinonen, J. Chem. Phys., 153 (2020),194113.

[2] Y. S. Al-Hamdani, P. R. Nagy, A. Zen, D. Barton, M. Kállay, J. G. Brandenburg, and A. Tkatchenko, Nature Communications, 12 (2021), 3927.

[3] T. Schäfer, A. Irmler, A. Gallo, and A. Grüneis, arXiv, physics, 2407.01442v3.

[4] Q. Ma and H.-J. Werner, WIREs Comput. Mol. Sci. e1371 (2018), 1.

[5] H.-J. Werner and A. Hansen, J. Phys. Chem. A 128 (2024), 10936.

IT-35: DFT: ADVANCES IN FUNCTIONAL APPROXIMATIONS AND IN THEORY FOR EXCITED STATES

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The foundations of density functional theory (DFT) for describing ground states were established by Hohenberg, Kohn, and Sham in 1964-1965. The accuracy of DFT predictions hinges on the quality of density functional approximations (DFAs). Despite advancements, significant systematic errors persist, such as underestimating energy gaps in molecules and materials, incorrectly predicting the dissociation limits of chemical bonds, overdelocalizing charge distributions, and misaligning energy levels at interfaces. These errors stem from the violation of exact conditions on fractional charges and spins, which are consequences of quantum mechanical degeneracy manifested in the classical variable of electron density. Recent advancements addressing these errors have elevated DFT to a new level of robustness and accuracy, broadening its applicability. Since the 1970s, Kohn-Sham functionals have been employed for ΔSCF calculations of excited states, achieving accuracy comparable to ground state results, despite a lack of theoretical justification. Recent research has established the theoretical foundation for ΔSCF calculations of excited states, showing that it is necessary to go beyond electron density and use the first-order density matrix of the noninteracting reference system to define the energy functional. The minimum of this functional corresponds to the ground state energy, consistent with ground state DFT, while the stationary solutions yield excited-state energies and electron densities, consistent with ΔSCF calculations.

[1] Cohen, A. J.; Mori-Sanchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. Science 2008, 321 (5890), 792–794.

IT-36: HOMOTOPY CONTINUATION METHOD FOR SOLVING DYSON EQUATION FULLY SELF-CONSISTENTLY

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Solution of the Dyson equation for the small-gap systems can be plagued by large non-converging iterations. In addition to the convergence issues, due to a high non-linearity, the Dyson equation may have multiple solutions. We apply the homotopy continuation approach to control the behavior of iterations. We used the homotopy continuation to locate multiple fully self-consistent GW solutions for NdNiO2 solid and to establish the corresponding Hartree-Fock limits. Some of the solutions found are qualitatively new and help to understand the nature of electron correlation in this material. We show that there are multiple low-energy charge-transfer solutions leading to a formation of charge-density waves. Our results qualitatively agree with the experimental conductivity measurements. To rationalize the structure of solutions, we compare the k-point occupations and generalize the concept of natural difference orbitals for correlated periodic solids.

IT-37: RESPONSE THEORY AND MOLECULAR INTERACTIONS

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This talk will highlight the significance of response theory in the study of molecular interactions. In the Warsaw Quantum Chemistry group, we developed a fully Hermitian formulation of Coupled Cluster theory using the expectation-value CC approach [1]. Building on this foundation, several new methodologies were introduced, notably the CCSD-based SAPT, which significantly improves the description of intramonomer correlation effects in the induction and dispersion interactions [2, 3] An important—though perhaps underappreciated—contribution by Jeziorski and collaborators was the direct calculation of some of the properties of the H_2 molecule (including relativistic corrections) without relying on the subtraction of monomer properties [4]. I will show how this concept can be incorporated into the SAPT framework to directly compute interaction-induced properties, such as the dipole moment of a van der Waals complex [5]. Furthermore, I will present how the new tool helps to understand how the electrostatic potential of the monomers should be corrected to account for Pauli exchange effects—an insight that leads to a new scheme for treating induction interactions to infinite order.

[1] Moszynski R., Zuchowski P. S., Jeziorski B., Time-independent coupled-cluster theory of the polarization propagator Coll. Czech Chem. Comm. 2005, 70(8) 1109.

[2] Korona T., Jeziorski B., Dispersion energy from density-fitted density susceptibilities of singles and doubles coupled cluster theory J. Chem. Phys. 2008, 128, 14, 144107.

[3] Zuchowski P., Moszynski R., Dispersion Energy from the Time-Independent Coupled-Cluster Polarization Propagator , J. Chem. Theory Comput. 2023, 19, 4, 1177–1185.

[4] Piszczatowski K., Lach G., Jeziorski B., Direct calculation of interaction-induced molecular properties Phys. Rev. A 77, 062514.

[5] Tyrcha B., Gupta T., Patkowski K., Zuchowski P. S. Analytical derivatives of symmetry-adapted perturbation theory corrections for interaction-induced properties J. Chem. Theory Comput. 2025, 21, 9, 4562.

NEW CHALLENGES FOR AB INITIO THEORY IN MOLECULAR SCIENCE

CONTRIBUTED TALKS

CT-1: ROVIBRATIONAL QUANTUM DYNAMICS OF SIMPLE VAN DER WAALS COMPLEXES

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The structure, rovibrational quantum dynamics, and spectroscopy of simple van der Waals dimers, formed by the diatomic molecules N_2 and CO, have been investigated. Most importantly, our high-level computations provide clear evidence about the complex structural, dynamical, and spectroscopic behavior of the dimers, which can be summarized in the statement that they are quasi-structural [1] species.

To fully understand the energy-level structure of the bound and unbound states of the dimers, several highly accurate potential energy surfaces (PES) have been generated, including, for the first time, full-dimensional (6D) PESs, constructed using symmetry-adapted perturbation theory (SAPT) and at least the CCSD(T) level of electronic-structure theory.The latter PESs clearly have spectroscopic accuracy. These PESs allow for the unambiguous identification and characterization of stationary points of different order. The most important stationary points have been characterized by the focal-point analysis approach [2].

Using exact kinetic energy operators and the best of these PESs, (quasi-)variational nuclear-motion computations were performed, computing many bound and quasi-bound rotational-vibrational states. While previous studies [3, 4] employing the rigid monomer approximation during the construction of reduced-dimensional PESs provided conflicting results, the increased accuracy and rigor of our approach enables us to confirm the presence of only a single, Z-shaped global minimum in the case of the N_2 dimer [5]. Since this minimum has four versions in the case of ($^{14}N_2$), the nuclear-motion computations were performed within the framework of the G16 molecular symmetry group, yielding symmetry labels for the computed states and enhancing their analysis. Similar results have been obtained for the CO dimer.

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[1] Császár, A. G., Fóbri, C. & Sarka, J. WIREs Comp. Mol. Sci. 10 (2019) e1432.

[2] Csószór, A. G., Allen, W. D. & Schaefer, H. F. J. Chem. Phys. 108 (1998) 9751.

[3] Hellmann, R. Mol. Phys. 111 (2013) 387.

[4] Berns, R. M. & van der Avoird, A. J. Chem. Phys. 72 (1980) 6107.

[5] Tóbiás, R., Fóbri, C., Bosquez, M., Kodrycka, M., Patkowski, K. & Csószór, A. G. Small Struct. (2025) submitted for publication.

CT-2: COMPLETE INSENSITIVITY TO *AB INITIO* DATA – A NEW PERSPECTIVE ON MODELING COLLISION-INDUCED ABSORPTION OF NOBLE GAS ATOMS

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When gas molecules interact through the van der Waals force, minute rearrangements of their normal charge distribution occur, resulting in interaction-induced dipole moment. This dipole moment allows the complex to absorb electromagnetic radiation, resulting in Collision Induced Absorption (CIA) spectra [1, 2]. In this study, we systematically investigate how the accuracy of CIA spectra depends on the quality of the *ab initio* data used. This study also reveals a previously unreported double-peak structure for the Ne–He complex. Our analysis shows that the range of internuclear distances relevant for CIA spectra varies with temperature, with short-range interactions becoming increasingly important at high temperatures. The long-range van der Waals induced dipoles never contribute. These findings provide new insights into the temperature-dependent behavior of CIA spectra and emphasize the importance of accurate modeling of short-range interactions for reliable astronomical modeling.

[1] Frommhold L., Collision-Induced Absorption in Gases, 2nd ed. (Cambridge University Press, Cambridge, England, 2006.

[2] Kiss Z. J. and Welsh H. L., Phys. Rev. Lett. 2 166, 1959.

CT-3: TOWARDS ACCURATE DESCRIPTION OF INTERMOLECULAR INDUCTION

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A key feature of Symmetry-Adapted Perturbation Theory (SAPT) [1] is the composition of interaction energy with physically significant terms such as: electrostatic, exchange, induction and dispersion. Among these, the induction energy plays a significant role, specially for strongly bonded systems. However, the induction terms in perturbation theory diverge and the low order terms do not recover the total induction. The missing higher order induction can be incorporated with $\delta_{\mathrm{int}}^{\mathrm{HF}}$ correction, resulting into a hybrid theory. While the $\delta_{\mathrm{int}}^{\mathrm{HF}}$ correction is important for H-bonded systems, but it is also known to overbind dispersion-dominated complexes. Therefore, it would be ideal to recover the induction effect in a consistent theory. One such approach is Pauli-Blockade (PB) [2] method, which offers a variational framework for infinite-order induction. However, because of the orthogonalisation step and subsequent loss of monomer identity, this theory is not useful for further SAPT-like development.

In this work, we explore intermolecular interactions through a variational approach termed as Symmetry-Adapted Relaxation Theory (SART), which is motivated by PB method but maintains monomer identity, therefore retaining SAPT-like character. Our methodology formulated in second quantization, is implemented using Psi4NumPy [3], a Python-based interface for the computational chemistry software Psi4. We report the agreement between interaction energy computed using our approach and supermolecular Hartree-Fock energy, demonstrating that variationally relaxed monomers effectively capture induction effects to infinite-order in the interaction operator.

[1] Jeziorski B., Moszynski R., Szalewicz K., Perturbation theory approach to intermolecular potential energy surfaces of van der Waals complexes, *Chemical Reviews* (1994).

[2] Rajchel Ł., Żuchowski P.S., Szczęśniak M. M., Chałasiński G., Density Functional Theory Approach to Noncovalent Interactions via Monomer Polarization and Pauli Blockade, *Phys. Rev. Lett. 104* (2010).

[3] Psi4NumPy: An Interactive Quantum Chemistry Programming Environment for Reference Implementations and Rapid Development, *J. Chem. Theory Comput.* (2018).

CT-4: QUANTUM-INFORMED MACHINE LEARNING FOR PREDICTING FLUORESCENCE QUANTUM YIELD

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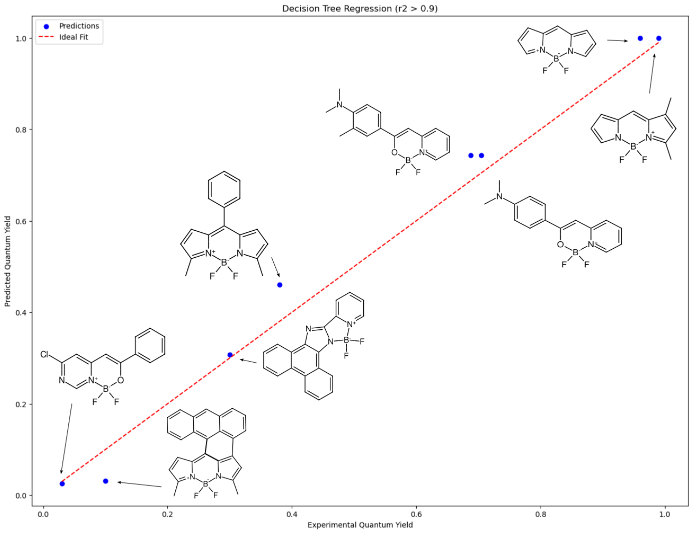
Machine learning (ML) provides a data-driven approach for predicting molecular properties at lower computational cost than first-principles methods [1]. Here, we present a quantum-informed ML framework to predict fluorescence quantum yields (Φ_{fl}) of neutral boron- and fluorine-containing organic molecules in methanol and chloroform [2]. Starting from a SMILES-encoded database, we generated optimized 3D geometries and computed ground- and excited-state properties using ORCA 6.0 at the ωB97X-D3/def2-TZVP level, including radiative decay rates via the ORCA excited state dynamics module [3]. Solvent effects were treated with a shell model using the SOLVATOR module of ORCA combined with GKS-EDA and its time-dependent extension GKS-EDA(TD) [4, 5]. The resulting quantum-chemical descriptors formed the basis of a bespoke dataset. We trained several models such as classification and regression trees, random forests, linear support-vector classifiers, and Lasso regression to predict Φ_{fl} directly. Preliminary results indicate that our leading ML model approaches the accuracy of experimental data while requiring less amount of computational time per molecule than full excited state dynamics—a promising sign of the method's efficiency. However, this work remains ongoing: we are currently expanding the dataset to include more systems, exploring new machine learning strategies, and integrating uncertainty quantification to better assess model reliability.



[1] Qi Ou; Qian Peng, and Zhigang Shuai. J. Phys. Chem. Lett., 11 (2020), 7790.

[2] Joung JF; Han M; Jeong M and Park S, Sci. Data. 7 (2020), 225.

[3] Psi4NumPy: An Interactive Quantum Chemistry Programming Ede Souza B; Neese F and Izsak R, J. Chem. Phys., 148 (2018), 034104.

[4] Su P; Tang Z and Wu W, WIREs Comput. Mol. Sci., 10 (2020), e1460.

[5] Tang Z; Shao B; Wu W and Su P, Phys. Chem. Chem. Phys., 25 (2023), 18139.

CT-5: SINGLE- AND MULTI-REFERENCE APPROACHES FOR OPEN-SHELL METAL CLUSTER–PAH INTERACTIONS. UMP2C AND RS2CC METHODS

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Accurate modeling of intermolecular interactions involving open-shell metal clusters remains a significant challenge in computational chemistry, particularly when large dispersion contributions and multireference effects coexist [1]. In this talk, two recent methodological advances will be presented – unrestricted coupled Møller-Plesset second-order perturbation theory (UMP2C) [2] and coupled internally contracted multistate multireference Rayleigh–Schrödinger second-order perturbation theory (RS2CC) [3] – designed to enhance the accuracy of wavefunction-based approaches for studying open-shell metal cluster–polycyclic aromatic hydrocarbon (PAH) interactions. UMP2C is based on the original MP2C approach of Heßelmann and Korona [4, 5] and a follow-up work on van-der-Waals dominated metal cluster-PAHs interactions [6]. The method refines conventional MP2 by replacing the uncoupled Hartree–Fock dispersion with a coupled dispersion correction, enabling accurate treatment of van der Waals (vdW) and beyond-vdW interactions in open-shell systems within a single-reference framework. Benchmarking against explicitly correlated coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)-F12] for Cu$_3$–PAH model systems demonstrates subchemical accuracy, making UMP2C a practical and reliable ab initio alternative to commonly used methods. [2] Complementing this, RS2CC approach introduces a dispersion correction into the RS2C method of Celani and Werner [7], enabling to address multireference problems effectively. RS2CC allows for consistent treatment of near-degeneracies and conical intersections [3]. Together, UMP2C and RS2CC provide a practical toolkit for addressing open-shell cluster–PAHs interactions, offering new insights into the characterization of supported catalysts on carbon-based surfaces and the design of materials at the quantum level.

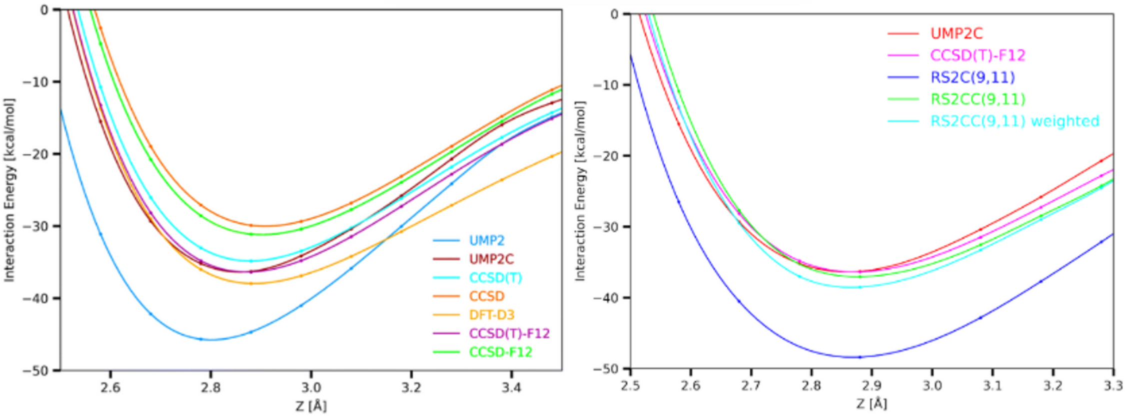

Figure 1: Interaction potentials for Cu3–benzene evaluated with the (A)VTZ(-PP) basis set. Left panel: results from DFT-D3, UMP2, UMP2C, CCSD, CCSD-F12, CCSD(T), and CCSD(T)-F12 methods. Right panel: Comparison of high-level methods including CCSD(T)–F12, UMP2C, RS2C(9,11), RS2CC(9,11), and RS2CC(9,11) weighted [2, 3].

[1] M.P. de Lara-Castells, Small Structures, 5 (2024), 202400147.
[2] K.M. Krupka, A. Krzemińska, M.P. de Lara-Castells, RSC Adv., 14 (2024), 31348–31359.
[3] K.M. Krupka, M.P. de Lara-Castells, Phys. Chem. Chem. Phys., 26 (2024), 28349–28360.
[4] A. Heßelmann, J. Chem. Phys., 128 (2008), 144112.
[5] A. Heßelmann, T. Korona, Phys. Chem. Chem. Phys., 13 (2011), 732–743.
[6] M. P. de Lara-Castells, A. O. Mitrushchenkov, H. Stoll, J. Chem. Phys., 143 (2015),102804.
[7] P. Celani and H.-J. Werner, J. Chem. Phys., 112 (2000), 5546–5557.

CT-6: AUTOMATIC TEMPERATURE-DEPENDENT LATTICE FREE ENERGIES OF DISORDERED MOLECULAR CRYSTALS

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In 1998, the drug ritonavir made headlines as million-dollar losses were caused by the failure to anticipate a more stable crystal packing (polymorph)[1]. In response, at Avant-garde Materials Simulation (AMS), we have developed software for Crystal Structure Prediction (CSP) to identify thermodynamically stable polymorphs for the past 20 years[2]. Nowadays, our predictions of lattice free energy landscapes of a compound are performed even as a function of temperature, pressure and relative humidity[3]. However, a new challenge has surfaced: around one in every ten experimental crystal structures is disordered, and every effect of configurational free energy needs to be considered. In the latest CSP blind test, the predicted structures for all seven compounds contained as many as four disordered crystal structures. Current tools allow us to deal with modest disorder, but the amount of approximations and manual labor this entails is impractical for routine purposes. Considering all possible ways to re-arrange molecules in a crystal generally leads to a combinatorial explosion. This is critical in the context of CSP, where thousands of crystals should undergo disorder analysis, and also because disorder leads to changes in the energy landscapes[4]. We have now established a classification of the molecular Degrees Of Freedom (DOFs) leading to disorder, based on disordered crystals from the Cambridge Structural Database. Additionally, we have created a new software module in AMS's GRACE suite[5] to automatically find said DOFs in a crystal, generate disorder models, and evaluate their configurational and vibrational free energy. Preliminary results suggest that the approach is not only able to identify disorder sites, but also to provide a quantitative description of thermal populations of disorder configurations along with lattice expansion. This represents a milestone in the modeling of disorder in molecular crystal structures, which, combined with CSP, provides us with better predictions of crystal energy landscapes.

[1] Bučar DK, Lancaster RW, Bernstein J. Disappearing polymorphs revisited. Angew Chem Int Ed Engl. 2015 Jun 8;54(24):6972-93.

[2] Neumann MA, Perrin MA. Energy ranking of molecular crystals using density functional theory calculations and an empirical van der waals correction. J Phys Chem B. 2005 Aug 18;109(32):15531-41.

[3] Firaha, D., Liu, Y.M., van de Streek, J. et al. Predicting crystal form stability under real-world conditions. Nature 623, 324–328 (2023).

[4] Dittrich B. On modelling disordered crystal structures through restraints from molecule-in-cluster computations, and distinguishing static and dynamic disorder. IUCrJ. 2021 Feb 18;8(Pt 2):305-318.

[5] Neumann MA. Tailor-made force fields for crystal-structure prediction. J Phys Chem B. 2008 Aug 14;112(32):9810-29.

CT-7: CUTTING-EDGE MACHINE LEARNING APPROACHES FOR EFFICIENT AND ACCURATE REACTION NETWORK ANALYSIS

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Accurately predicting reaction barrier heights associated with transition state structures is essential for understanding chemical reactivity across diverse domains such as combustion chemistry, astrochemistry, and catalysis. Traditional computational approaches, including high-level electronic structure methods, offer high accuracy but are prohibitively expensive for large or complex reaction networks.

To address this limitation, we explore the use of neural networks, specifically the MACE architecture [1], an equivariant message-passing neural network (MPNN), that employs higher-order interactions to deliver state-of-the-art accuracy with remarkable computational efficiency. While MACE was originally designed to improve force fields, our work extends its application toward chemical reactivity, with the specific goal of directly predicting accurate barrier heights at a low computational cost.

Preliminary results, based on training these machine learning models on a curated dataset of over 11 thousand reactions, show promising performance, positioning machine learning as a robust alternative to semiempirical quantum mechanical (SQM) corrections or conventional DFT-based workflows.

Our ongoing efforts focus not only on training purely machine learning models that do not rely on SQM methods, but also on exploring Δ-ML approaches that learn the differences between SQM and reference DFT data. The goal is to enable accurate and efficient prediction of transition state properties, paving the way for rapid and scalable exploration of reaction networks. This approach has the potential to significantly advance the field of chemical kinetics by balancing computational feasibility with predictive accuracy.

[1] I. Batatia, D. P. Kovács, G. N. C. Simm, C. Ortner, G. Csányi, Advances in Neural Information Processing Systems, 35 (2022), 11423-11436.

CT-8: SYMMETRY-ADAPTED RELAXATION THEORY (SART): FIRST-QUANTIZATION HARTREE-FOCK THEORY AND IMPLEMENTATION

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Symmetry-adapted relaxation theory (SART) is a variational approach that provides an infinite-order treatment of monomer relaxation effects in intermolecular complexes. Unlike per- turbative frameworks, SART directly optimizes each monomer wavefunction in response to the interaction electrostatic and full exchange potential [1] of the partner, ensuring a self-consistent determination of energy contributions, while maintaining a SAPT-like non-orthogonality between the monomer spaces. That is, monomer identities are retained, allowing for a SAPT-like decomposition of the interaction energies, derived directly from the SART wave- function.

We present the first-quantization formulation of SART[HF], denoted as FQ-SART[HF], which reformulates the second-quantized theory, SQ-SART[HF], without introducing explicit ap- proximations of the antisymmetrization operator in powers of overlap-matrix S. The method inherently achieves an exact antisymmetrization of the supramolecular wavefunction. This provides a more accurate and physically consistent representation of monomer relaxation while maintain- ing exact energy calculations equivalent to fully relaxed supermolecular Hartree–Fock solutions.

Following the theoretical discussion, we present the results of our implementation of FQ- SART[HF] as a PSI4-compatible Python module, showcasing its computational efficiency and accuracy compared to conventional methods.

Finally, we discuss future perspectives, including the systematic implementation of regularization techniques to separate charge delocalization (CD) and polarization (POL) contributions [2], and the extension toward SART[DFT] to improve physical accuracy and ap- plicability to correlated electronic structure methods.

[1] B. Jeziorski, M. Bulski, and L. Piela, First-order perturbation treatment of the short-range repulsion in a system of many closed-shell atoms or molecules, International Journal of Quan- tum Chemistry, 10(2):281–297 (1976).

[2] A. J. Misquitta, Charge transfer from regularized symmetry-adapted perturbation theory, Journal of Chemical Theory and Computation, 9(12):5313–5326 (2013).

CT-9: NEW APPROACH FOR DISTRIBUTED MULTIPOLE ASSESSMENT: WHY YOU SHOULD USE LISA

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Intermolecular force fields rely on interaction terms between atomic sites. The interaction strength depends on parameters assigned to each site according to their chemical identity. Since such distributed properties are non-observable their choice appears arbitrary. On the other hand, the proposed derivation schemes differ in simplicity, transferability, and accuracy. This talk will rationalize the choice of electrostatic multipolar model for force field development and machine learning. Intermolecular interactions are shaped by anisotropies in the electron density. This can be abstracted by a series of tensors with increasing angular complexity, the multipole expansion. Fast convergence of the multipolar series is desired, allowing the omission of high-ranking moments without compromise on accuracy. We introduce a general benchmarking procedure for multipolar methods that accurately resolves the convergence of the potential with multipolar rank. Moreover, our approach infers the nature of the charge penetration term. We will present quantitative error estimates as a function of both rank and distance for selected methods.

The Iterative Stockholder Algorithm (ISA) yields a rapidly convergent multipolar expan- sions due to a density partitioning into maximally spherical parts [1]. Multiple flavours of the ISA have emerged, in particular MBIS, BS-ISA, and the novel LISA [2, 3, 4]. Based on a chemically varied test set of 350 compounds, we demonstrate that any ISA flavor outperforms the GDMA unambiguously in rank convergence and physicality of the charge penetration term [5]. Our results indicate that through inclusion of octopoles, our models approach sub-kJ accuracy without further tuning. The novel LISA systematically outperforms the MBIS and BSISA method, and we strongly recommend LISA for force field and database design.

[1] T.C. Lillestolen, R.J. Wheatley, J. Chem. Phys., 131(14) (2009).

[2] T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Spey- broeck, M. Waroquier, P.W. Ayers, J. Chem. Theory Comput., 12(8) (2016), 3894.

[3] A.J. Misquitta, A.J. Stone, Theoretical Chemistry Accounts, 137(11) (2018), 153.

[4] Y. Cheng, E. Cancès, V. Ehrlacher, A.J. Misquitta, B. Stamm, J. Chem. Phys., 162(7) (2025).

[5] A. J. Misquitta, Charge transfer from regularized symmetry-adapted perturbation theory, Journal of Chemical Theory and Computation, 9(12):5313–5326 (2013).

NEW CHALLENGES FOR AB INITIO THEORY IN MOLECULAR SCIENCE

POSTERS

NEW CHALLENGES FOR AB INITIO THEORY IN MOLECULAR SCIENCE

POSTER SESSION I

P-1: COMPUTATIONAL RIXS: BENCHMARK AND APPLICATIONS TO ORGANIC MOLECULES USED IN PHOTOVOLTAICS

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Resonant inelastic X-ray scattering (RIXS) has attracted attention in recent years because it can provide an element, orbital, and site-selective mapping of valence excitations in molecules or solids [1]. RIXS can be viewed as a two-step process, where the resonant absorption of an X-ray photon is followed by an inelastic radiative de-excitation from the intermediate core-excited state to a final valence-excited state. The element, orbital, and site specificity of RIXS derives from the very large energy separation between different types of core-excitations and their highly localized nature. RIXS spectra and two-dimensional (2D) RIXS maps contain a wealth of information which can be accessed given accurate computational models. Here, we will introduce two approaches to determine electronic RIXS spectra of molecular systems. We will focus on linear response time-dependent density functional theory (LR-TDDFT), which provides an inexpensive approach to modeling RIXS for molecules, as well as the algebraic diagrammatic construction scheme for the polarization propagator (ADC). ADC is a Green's function based method with accuracies on par with the coupled cluster (CC) hierarchy when it comes to the description of core [2] and valence-excitations [3]. Different DFT functionals, including generalized gradient approximation (GGA), hybrid, range-separated, and tailored functionals, will be benchmarked against ADC for a set of small molecules at the C, N, and O K-edges. The application of LR-TDDFT in the computation of RIXS of selected organic molecules used in photovoltaics will be illustrated for the best performing functionals in the benchmark set.

[1] F. M. F. de Groot, M. W. Haverkort, H. Elnaggar, A. Juhin, K.-J. Zhou, P. Glatzel, Nat. Rev. Methods Primers, 4 (2024), 45.

[2] T. Fransson, I. E. Brumboiu, M. L. Vidal, P. Norman, S. Coriano, A. Dreuw, J. Chem. Theory Comput., 17 (2021), 1618–1637.

[3] A. Dreuw, M. Wormit, WIREs Comput. Mol. Sci., 5 (2015), 82–95.

P-2: LONG-RANGE DISPERSION INTERACTION BETWEEN ATOMS AND MOLECULES IN ELECTRONICALLY EXCITED STATES

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Dipole polarizability is a fundamental property that governs a system's response to external electric fields, shaping its optical characteristics, dielectric behavior, and van-der-Waals interactions. The C_6 dispersion coefficient, derived from frequency-dependent polarizability, plays a pivotal role in quantifying long-range intermolecular forces. While ground-state polarizabilities are well-characterized, the accurate and efficient prediction of excited-state polarizabilities remains a significant computational challenge.

In this work, we investigate excited-state dynamic polarizabilities evaluated at imaginary frequencies and compute the corresponding C_6 isotopic dispersion coefficients using an expectation-value approach within the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) framework, as available in the Q-Chem software package. In contrast to conventional response theory, this expectation-value formulation offers substantial reductions in both computational cost and memory requirements, while preserving the high accuracy of the results.

We apply this approach to a set of atomic and molecular systems - including He, Ne, Ar, H_2, N_2, CO, and benzene (C_6H_6) - demonstrating its effectiveness in accurately and efficiently computing excited-state dispersion coefficients. This work establishes the expectation-value formalism as a reliable and scalable method for excited-state polarizability calculations, with broad applicability to the study of intermolecular interactions and electronic structure in excited states.

P-3: FIRST-ORDER SYMMETRY-ADAPTED PERTURBATION THEORY WITH DOUBLE EXCHANGE FOR MULTIREFERENCE SYSTEMS

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We extend first-order multiconfigurational symmetry-adapted perturbation theory [1], to account for double-exchange effects, where up to two electron pairs are exchanged between the monomers [2]. To achieve this, we derive density-matrix-based expressions for the first-order exchange energy to arbitrary orders in the overlap expansion. As a numerical demonstration, we apply the double-exchange approximation to strongly orthogonal geminal wave functions. Additionally, we propose an approximate method for evaluating S^4 exchange energy with complete active space (CAS) wave functions of the valence type, i.e., with n active electrons distributed over n orbitals. We demonstrate the performance of these methods on model dimers in both ground and excited states. Moreover, we show that the connectedness of the first-order exchange energy relies on the vanishing property of the derivative of the chromatic polynomial $\chi'_G(0)$ for disjoint graphs.

[1] M. Hapka, M. Przybytek, and K. Pernal, J. Chem. Theory Comput. 17.9 (2021), pp. 5538-5555.

[2] D. Cieśliński, M. Przybytek, G. Chałasiński, M. Hapka, arXiv:2504.13585.

P-4: ADVANCING QUANTUM EMBEDDING METHODS FOR MODELING CATALYTIC ENVIRONMENTS: LOCAL APPROXIMATIONS AND FORCES

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The thermochemical modeling of complex reactions require accurate and fast quantum chemical methods. If the chemical change is localized to a small part of the system, with embedding methods, an accurate high-level method can be applied for the chemically active region and a more efficient approach for the environment. Here, we report extensive acceleration of our Huzinaga-equation-based embedding [1] via local approximations to wavefunction (WF) and density functional theory (DFT) based WF-in-DFT and DFT-in-DFT embedding using density fitting. Namely, both the atomic orbital and auxiliary basis sets are restricted exploiting the locality of the active occupied orbitals [2]. Near hybrid DFT accuracy can be achieved at computational cost similar to that of a generalized gradient approximation (GGA) DFT calculation. We tested the new approaches on homogeneous, surface and enzyme catalytic reactions showing a few tenths kcal/mol error compared to complete (non-embedding) hybrid DFT calculations with 30–90-fold speedup. In addition, we implemented analytic gradients [3] for the Huzinaga-equation-based embedding where second-order Møller–Plesset perturbation theory or (double) hybrid DFT is used for the active region and GGA or hybrid DFT for the environment. We show that bond lengths and angles converge rapidly with the size of the embedded system. Our approach has the potential to relax the coordinates of the environment, while it provides structural parameters close to high-level quality for the embedded atoms. Calculations on a 171-atom zeolite and a 570-atom protein system show that the Huzinaga-equation-based embedding can accelerate (double) hybrid force evaluations by an order of magnitude and enables affordable geometry optimization for molecules of hundreds of atoms. The code is available in the MRCC program package for free of charge for academic user [4].

[1] B. Hégely, P. R. Nagy, Gy. G. Ferenczy and M Kállay, J. Chem. Phys., 145 (2016) 064107.

[2] J. Csóka, D. Berta, P. R. Nagy, J. Phys. Chem. Lett., submitted (2025).

[3] J. Csóka, B. Hégely, P. R. Nagy and M. Kállay, J. Chem. Phys., 160 (2024) 124113.

[4] D. Mester, P. R. Nagy, J. Csóka, L. Gyevi-Nagy, P. B. Szabó, R. A. Horváth, K. Petrov, B. Hégely, B. Ladóczki, Gy. Samu, B. D. Lőrincz, and M. Kállay, J. Phys. Chem. A, 129 (2025) 2086.

P-5: THEORETICAL PREDICTION OF MAGNETO-CHIRAL DICHROISM FOR HELICENES AND OTHER CHIRAL ORGANIC MOLECULES

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Magneto-chiral dichroism (MChD) is a unique chiroptical effect observed in chiral systems within a magnetic field, offering insights into molecular properties and fundamental light-matter interactions [1, 2]. We present extensive theoretical predictions of MChD spectra, alongside electronic circular dichroism (ECD) and magnetic circular dichroism (MCD), for diverse chiral organic molecules [3]. Investigated systems include carbo[n]helicenes ([3]- to [8]-helicene) and smaller chiral molecules like propylene oxide, substituted cyclopropanones, and 3-(trifluoroacetyl)-camphor.

MChD properties were computed using complex (damped) quadratic response theory, primarily with the B3LYP functional and aug-cc-pVDZ basis set in the DALTON program suite [4]. A wavelength scaling procedure, benchmarked against available experimental ECD/MCD data, was applied to refine MChD predictions.

This study delivers the first comprehensive set of MChD spectral predictions for these molecular series. For larger helicenes ([6]-, [7]-, and [8]-helicene), MChD dissymmetry factors (g_{MChD}) are predicted around 10^{-6}, suggesting experimental feasibility, with signal strength generally increasing with helicene size. Smaller systems also exhibit distinct predicted MChD features. The agreement with available ECD and MCD experiments is good.

These theoretical benchmarks across varied chiral molecules aim to guide experimental MChD spectroscopy, highlighting molecular features influencing MChD signals and the utility of computational modeling for this complex phenomenon.

[1] L. D. Barron and J. Vrbancich, Mol. Phys., 51 (1984) 715-730.

[2] G. L. J. A. Rikken and E. Raupach, Nature, 390 (1997) 493-494.

[3] S. Coriani, M. Pecul, A. Rizzo, P. Jørgensen, M. Jaszuński, J. Chem. Phys., 117 (2002) 6417-6428.

[4] J. Cukras, J. Johansson, P. Norman, A. Rizzo, G. Rikken, S. Coriani, Phys. Chem. Chem. Phys., 18 (2016) 13267-13279.

P-6: THE EXCITED ELECTRONIC STATES OF THE HELIUM DIMER INCLUDING ADIABATIC AND RELATIVISTIC EFFECTS

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Background The helium dimer serves as an exemplary system for advancing our understanding of few-body physics, high-resolution laser spectroscopy, and the properties of ultracold molecules. Unparalleled accuracy has been achieved for He_2 in the ground state [1], setting a global benchmark. In contrast, excited states remain significantly less explored, with existing *in silico* studies achieving only a reasonable level of accuracy. Previous computations of excited states [2] deviate from experimental results by approximately 1.5%, which remains insufficient for reliably guiding and interpreting cutting-edge spectroscopic experiments. Highly accurate *ab initio* results not only allow for a direct comparison with experimental data but also guide upcoming experiments and pave the way towards the verification of the Standard Model.

Purpose This study aims to achieve benchmark-quality potential energy curves (PECs) with the highest possible accuracy for the few lowest excited states of the helium molecule. We systematically explore these states using various methods and basis sets to provide a reliable estimate of the accuracy of our computations. After incorporating relativistic and adiabatic corrections, we achieve an exceptional level of accuracy, which is essential for guiding ongoing experiments.

Method We utilize an extensive range of molecular electronic structure theory methods, including coupled cluster approaches (CCSD(T), CCSDT, EOM-CCSD, EOM-CC3) and configuration interaction (Full CI) methods. Our calculations employ basis sets developed for the He(^{1}S) + He($_3$S) states with cardinal numbers up to 10Z, with results extrapolated to the complete basis set limit.

Results Potential energy curves (PECs) are calculated for interatomic distances up to 50 a_0. The states from the first four asymptotes are computed using the Full CI method with basis sets up to 7Z and various coupled cluster methods with basis sets up to 8Z. Additionally, a single-point calculation for the $\mathrm{a}^3\Sigma_\mathrm{u}^+$ and $\mathrm{c}^3\Sigma_\mathrm{g}^+$ states is provided up to the 8Z basis set using Full CI, and up to the 10Z basis set using EOM-CC3 to demonstrate convergence at the global minimum. Our calculations achieve a theoretical accuracy reaching **1.0 cm^{-1} (60–200 ppm)** at the minimum.

Conclusions The results of our calculations provide highly accurate data, enabling the calculation of Franck-Condon factors for higher Rydberg states of the helium dimer or the helium molecular ion. We report that our study has achieved the highest accuracy for the helium dimer in excited electronic states.

[1] M. Przybytek, B. Jeziorski *et al*, *Phys. Rev. Lett*, 119 (2017), 123401.
[2] M. Pavanello *et al*, *Int. J. Quantum Chem*, 108 (2008), 2291-2298.

P-7: A NEW PERTURBATIVE TRIPLES CORRECTION SCHEME TO UNITARY COUPLED CLUSTER METHOD

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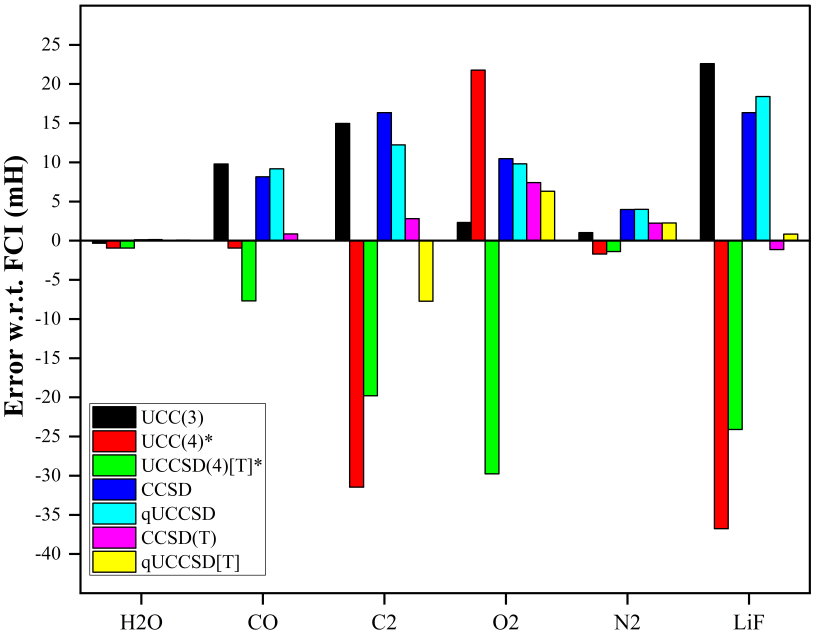
We present a new perturbative triples correction scheme for the quadratic unitary coupled cluster (qUCCSD) method. The method uses a projection-based approximation based on Bernoulli numbers to arrive at a size-extensive implementation of the unitary coupled cluster method [1]. The new triples perturbative correction(qUCCSD[T]) scheme can be derived from a simple perturbation truncation to the projection-based unitary coupled cluster energy functional and gives superior performance than the previously available partial triples correction scheme to unitary coupled cluster methods on a classical computer [2]. The performance of the method has been tested for binding energy, bond length, harmonic frequency, ionization potential, and electron affinity of small molecules containing heavy elements, and its performance has been found to be comparable to the standard CCSD(T) method.



JS and AKD acknowledge support from EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00117.

[1] K. Majee, S. Chakraborty, T. Mukhopadhyay, M.K. Nayak, and A.K. Dutta, J. Chem. Phys., 161 (2024) 034101.

[2] J. W. Windom, D. Claudino, and R.J. Bartlett, J. Chem. Phys., 160 (2024) 214180.

P-8: MOLECULAR ORBITAL PAIR CONTRIBUTIONS TO THE EXCHANGE REPULSION ENERGY EXPLAIN THE CONUNDRUM OF π-INTERACTIONS

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While accurate and efficient approaches are well established for the evaluation of intermolecular interactions of π-systems, their interpretation and understanding is a persistent problem. Recent [1] (and not so recent [2]) work indicate that exchange repulsion has a significant effect on the aggregate structure of planar π-stacked systems which is due to its (poorly understood) anisotropic behaviour.

We present a model which partitions the exchange repulsion energy, E_{xr}, between two closed shell systems A and B into orbital pair contributions to the exchange energy, $E_{\text{xr}}(a,b)$, where a and b represent Hartree-Fock orbitals of the respective systems [3, 4]. For π-orbitals, these contributions are shown to be essentially proportional to the squared overlap integral $|(a|b)|^2$. For slip-stacked motions of one of the π-systems, $E_{\text{xr}}(a,b)$ is thus mapping spatial oscillations of the wave functions a and b.

We demonstrate that the $E_{\text{xr}}(a,b)$ terms rationalize the oscillatory structure of the intermolecular potentials of acene dimers and of donor-acceptor complexes. For constant distance between the molecular planes, the energetically most favourable structures are found for arrangements with *small* exchange repulsion energies. Similar structures are observed in experimental crystal and aggregate structures. We do also explain that these structures get particularly *high* exchange repulsion energies if the interaction energy is optimized with respect to the interplanar distance.

We conclude that, wave function properties of molecular orbitals are mapped in intermolecular potentials of π-stacked systems and that these should be included in the interpretation and modelling of intermolecular potential energy surfaces.

[1] K. Carter-Fenk and J. M. Herbert, Chem. Sci., 11 (2020) 6758. *ibid.* Phys. Chem. Chem. Phys., 22 (2020) 24870.

[2] S. L. Price and A. J. Stone, Mol. Phys., 47 (1982) 1457.

[3] J. Henrichsmeyer, M. Thelen, M. Bröckel, M. Fadel, S. Behnle, M. Sekkal-Rahal, and R. F. Fink, ChemPhysChem, (2023) e202300097.

[4] J. Henrichsmeyer, M. Thelen, and R. F. Fink, ChemPhysChem, (2024) e202400887.

P-9: A DOMAIN-BASED CHARGE-TRANSFER ANALYSIS OF THE FIRST EXCITED STATE CALCULATED WITH EOM-PCCD+S

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We introduce a new domain-based charge-transfer analysis tool[1, 2], applied to the first excited state of several dye molecules proposed as prototypical sensitizers[3] for dye-sensitized solar cells. The energies of the lowest-lying excited states were computed using the EOM-pCCD+S method and compared against various Density Functional Approximations (DFAs) and the Domain-based Local Pair Natural Orbital variant of Coupled Cluster Singles and Doubles (DLPNO-CCSD).

A unique feature of the proposed model is its ability to both quantify and trace the direction of charge flow between different molecular regions or moieties. This is achieved by analyzing the weights of the c_i coefficients contributed to excitations in the EOM-pCCD+S excited state, using the optimized, naturally localized pCCD orbitals.

These excitation contributions were further classified according to the molecular domain (donor, bridge, or acceptor) and the excitation type (local vs. charge transfer). The resulting hole and particle character for each domain was then compared to the corresponding analysis based on the transition density matrix[4], obtained from TD-CAM-B3LYP.

[1] L. Szczuczko, M. Gałyńska, M. H. Kriebel, P. Tecmer, K. Boguslawski, J. Chem. Theory and Comp., 21 (2025), 4506-4519.

[2] P. Tecmer, M. Gałyńska, L. Szczuczko, K. Boguslawski, J. Phys. Chem. Lett. 14 (2023), 9909-9917.

[3] T. Delgado-Montiel, J. Baldenebro-López, R. Soto-Rojo, D. Glossman-Mitnik, Molecules, 25 (2020), 3670.

[4] F. Plasser, J. Chem. Phys. 152, (2020), 084108 (2020).

P-10: INTERACTIONS OF ATOMIC IONS WITH DIATOMIC MOLECULES

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We investigate interactions of alkaline-earth atomic ions Ca^+ and Sr^+ with diatomic molecules: NH, OH, CO, NO, N_2, and O_2, some of which have nonzero angular momentum projection quantum number Λ in their ground electronic states. We employ state-of-the-art methods of quantum chemistry: CCSD(T) method with small-core effective core potentials. We use aug-cc-pwCVXZ-PP bases for the Ca and Sr, and aug-cc-pVXZ bases for other atoms, $X \in \mathrm{D}, \mathrm{T}, \mathrm{Q}, 5$. We also use mid-bond orbitals to accelerate the basis-set convergence of the interaction energy. We test our approach using all-electron Douglas-Kroll-Hess calculations instead of the ECP, and calculating the effect of full triple excitations for selected systems in selected basis sets. Among the investigated systems, the interaction energy minima of the Ca^+ complexes are deeper than those of the corresponding Sr^+ complexes (by about 10–20%). The Ca^+–N_2 potential is highly anisotropic, with a relatively deep minimum for the linear geometry, and a shallow minimum and a barrier for the T-shape geometry. Furthermore, this potential has an unexpectedly strong dependence on the nitrogen-nitrogen distance: change of r_{NN} by 3% leads to a change of about 20% in the depth of the potential energy curve for the linear geometry. Apart from the electronic structure calculations, we derive the multipole expansion of the interaction energy of an atomic ion with a $\Lambda \neq 0$ molecule up to the R^{-6} contributions. Interaction with the ion removes the degeneracy of the electronic terms of molecules in $\Lambda \neq 0$ states. The resulting interaction energies are obtained as the eigenvalues of a 2×2 perturbation matrix. The off-diagonal (with respect to the asymptotic states) terms appear for the first time for $n = 1 + 2\Lambda$, $n = 2 + 2\Lambda$, and $n = 4 + 2\Lambda$ in case of the multipole expansion of electrostatic, induction, and dispersion energies, respectively, where n gives the asymptotic decay rate of the given energy contribution, R^{-n}.

[1] B. Jeziorski, R. Moszyński, and K. Szalewicz, Chem. Rev., 94 (1994), 1887.

[2] W. Skomorowski and R. Moszyński, J. Chem. Phys., 134 (2011), 124117.

[3] G. C. Nielson, G. A. Parker, and R. T. Pack, J. Chem. Phys. (1976), 64 , 2055.

[4] R. P. Leavitt, J. Chem. Phys. 72 (1980), 3472.

[5] P. Piecuch, Int. J. Quant. Chem., 25 (1984), 449.

[6] P. E. S. Wormer, F. Mulder, and A. van der Avoird, Int. J. Quant. Chem., 11 (1977), 959.

P-11: THE ELECTRONIC STRUCTURE OF ALF MOLECULE

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Aluminum monofluoride (AlF) is an excellent molecule for ultracold experiments due to its high chemical stability and nearly diagonal Franck-Condon factors between the ground and selected excited states. Still, the precise design of cutting-edge experiments requires detailed knowledge of molecular properties, obtained either through spectroscopy or high-level electronic structure calculations. In this work, we provide a comprehensive characterization of the AlF molecule using *ab initio* methods.

First, we performed a systematic analysis of the electronic structure of AlF using various flavors of the equation-of-motion coupled-cluster (EOM-CC) method. We investigated the singlet, triplet, and quintet states of AlF up to 70,000 cm^{-1} above the ground state. Our study not only reproduced the positions of experimentally known states but also identified previously unobserved states at higher energies than those measured to date. Additionally, we computed the potential energy curves for the corresponding ions.

High-accuracy potential energy curves are presented for the $X^1\Sigma^+$ and a$^3\Pi$ states. We employed extensive basis sets to approach the complete basis set (CBS) limit and carefully analyzed the convergence of the energy with respect to the level of excitation included in the coupled-cluster wavefunction. Furthermore, we paid particular attention to non-adiabatic, relativistic, and quantum electrodynamic (QED) effects. We found that both QED and non-adiabatic corrections exceed the resolution of typical spectroscopic experiments. By assessing the convergence of each contribution with respect to basis set size, we achieved estimated uncertainties of 6 MHz for rotational constants and 0.6 cm^{-1} for vibrational frequencies, illustrating the current precision limits of theoretical methods.

In addition, we computed hyperfine interaction parameters for both the $X^1\Sigma^+$ and a$^3\Pi$ states, demonstrating rapid convergence with respect to the electronic wavefunction accuracy. Finally, we report the electric properties of AlF, including the permanent dipole moment as well as both static and dynamic polarizabilities.

P-12: INDUCTION ENERGY FOR MOLECULES IN EXCITED STATE – A COMPARISON OF INDUCTION ENERGY FROM FINITE-FIELD AND SAPT

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The induction energy is one of the component of interaction energy, which is tremendously difficult to calculate for molecules in their excited state (ES). For many years there was no methodology to use Symmetry Adapted Perturbation Theory (SAPT) [1] for calculating induction energy of molecules in ES. Recently, such possibility became available due to work from research group of Michał Hapka from University of Warsaw and Katarzyna Pernal from Lodz University of Technology called SAPT(MC). [2, 3] which can calculate induction energy in ES. However, there is possibility to calculate induction energies in ES using Finite Field approach given that one can obtain ES energies of a given monomer in presence of other monomer, which is the difficult part.

We have calculated induction energies from second derivative of ES energies in presence of field from other monomer. While for the SAPT calculation we have selected SAPT(UHF) [4] with the Maximum Overlap Method (MOM), [5] and SAPT(MC). SAPT(UHF) for the ES leverages non-aufbau orbitals derived from MOM, allowing it to effectively handle cases of broken spin symmetry. Remarkably, SAPT(UHF) shows a high level of agreement with SAPT(MC), demonstrating its accuracy for interaction energies even in cases of ES. Our study will attempt to benchmark the Induction energy of molecules in ES using Finite Field approach to determine the best suitable method for describing the ES property, ultimately contributing to the development of method under the formalism of SAPT for ES.

[1] R. Moszyński and S. Cybulski, J. Chem. Phys., 100 (1994), 4998–5010.

[2] M.R. Jangrouei, A. Krzemińska, M. Hapka, E. Pastorczak and K. Pernal, J. Chem. Theory Comput., 18 (2022), 3497–3511.

[3] K. Pernal, M. Hapka, M. Przybytek, M. Modrzejewski, A. Sokół and A. Tucholska, GammCor code, GitHub repository, https://github.com/pernalk/GAMMCOR (2023).

[4] D.G. Smith, L.A. Burns, A.C. Simmonett, R.M. Parrish, M.C. Schieber, R. Galvelis, P. Kraus, H. Kruse, R. Di Remigio, A. Alenaizan and A.M. James, J. Phys. Chem. A, 152 (2020), 18.

[5] A.T. Gilbert, N.A. Besley and P.M. Gill, J. Phys. Chem. A, 112 (2008), 13164–13171.

P-13: EFFECTS OF BASE STACKING ON EXCITED STATES IN NUCLEOBASES

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It is well established that base stacking interactions influence the excited-states of nucleobases [1]. However, the precise relationship between base overlap and photoinduced electron transfer remains insufficiently understood [2]. To investigate stacking patterns in nucleic acids, we developed and implemented a novel algorithm based on the geometric area of base overlap. The algorithm was applied to a series of adenine (A)–guanine (G) stacked geometries exhibiting varied overlap configurations. For each structure, vertical excitation energies were computed using the ADC(2)/cc-pVTZ method. Furthermore, the non-adiabatic coupling between the locally excited πGπG* and the charge transfer πGπA* states was analyzed using the Generalized Mulliken–Hush (GMH) approach and Boys localization method. The results provide valuable insights into the relation between base overlap and excited-state properties.

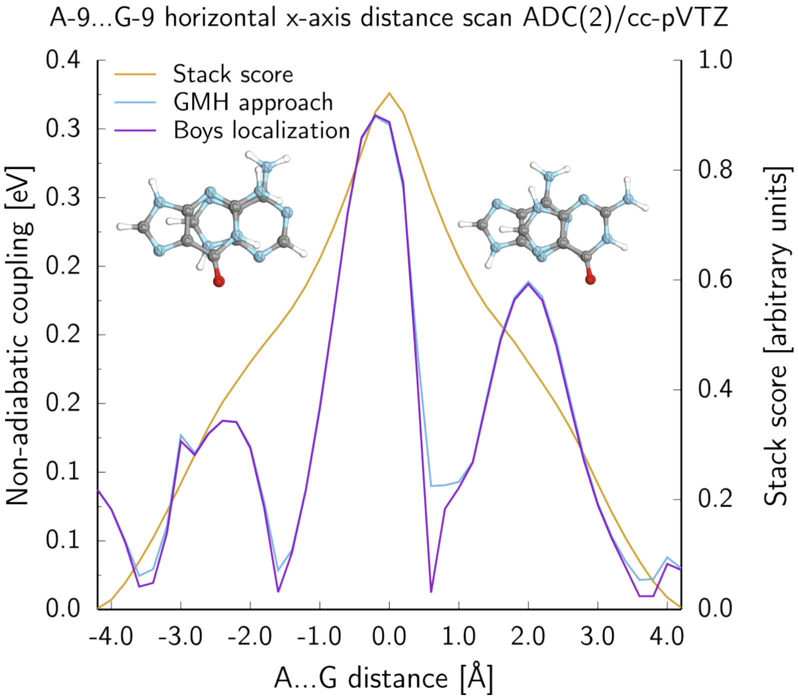

Figure 1: Non-adiabatic coupling estimated for the horizontal overlap scan.

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[1] C. L. Kufner et al., Chem. Sci., 15 (2024) 2158-2166.

[2] V. Petropoulos et al., Biomolecules, 14 (2024), 1548.

P-14: CORRECTING BASIS SET INCOMPLETENESS IN WAVE FUNCTION CORRELATION ENERGY BY DRESSING ELECTRONIC HAMILTONIAN WITH AN EFFECTIVE SHORT-RANGE INTERACTION

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We propose a general approach to reducing basis set incompleteness error in electron correlation energy calculations [1]. The correction is computed alongside the correlation energy in a single calculation by modifying the electron interaction operator with an effective short-range electron-electron interaction. Our approach is based on a local mapping between the Coulomb operator projected onto a finite basis and a long-range interaction represented by the error function with a local range-separated parameter, originally introduced by Giner et al. [2]. Unlike the basis set incompleteness error correction proposed in that work, our method does not rely on short-range correlation density functionals. As a numerical demonstration, we apply the method with complete active space wavefunctions. Correlation energies are computed using two distinct approaches: the linearized adiabatic connection (AC0) method [3] and n-electron valence state second-order perturbation theory (NEVPT2) [4]. We obtain encouraging results for the relative energies of test molecules, with accuracy in a triple-ζ basis set comparable to or exceeding that of uncorrected AC0 or NEVPT2 energies in a quintuple-ζ basis set.

[1] M. Hapka, A. Tucholska, M. M. Modrzejewski, P. Golub, L. Veis, K. Pernal, arXiv:2504.07192.

[2] E. Giner, B. Pradines, A. Ferté, R. Assaraf, A. Savin, J. Toulouse, J. Chem. Phys. 149, (2018), 194301.

[3] K. Pernal, Phys. Rev. Lett. 120 (2018), 013001.

[4] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, J. Chem. Phys. 114, (2001), 10252–10264.

P-15: DESCRIBING DISORDER AND CORRELATION – COHERENT POTENTIAL APPROXIMATION WITH BLOCH GAUSSIANS

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Doping and disorder have become powerful tools for manipulating material properties, such as in semiconductors, as well as for inducing emergent behavior beyond the sum of its constituent effects, e.g., in high-entropy alloys. Simulating the electronic structure of disordered systems typically demands large supercells, which is computationally expensive. The coherent potential approximation (CPA) offers an efficient alternative by introducing an effective medium that averages the effect of a disordered environment around a given atomic site. Existing *ab initio* CPA methods are largely constrained by the atomic sphere and single-site approximations, which express the nonlinear exchange-correlation potential as a sum of site-specific contributions. These approximations often oversimplify electronic interactions, limiting CPA's applicability beyond mean-field theories. Here, we present a novel implementation of CPA within first-principles density functional theory to study disorder effects in extended materials. By leveraging a modified approach based on Bloch Gaussian orbitals, we systematically improve the treatment of electron correlation. Our implementation represents a significant theoretical advancement, broadening the applicability of CPA to disorder-driven material design.

P-16: INSIGHTS INTO ROTATIONAL (DE-)EXCITATION OF INTERSTELLAR CALCIUM DICARBIDE (c-CaC_2) INDUCED BY HELIUM COLLISIONS

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Calcium dicarbide (CaC_2) is a promising candidate for detection in carbon-rich circumstellar environments due to the high cosmic abundance of calcium. Understanding its distribution, excitation, and abundance could provide valuable insights into processes that are not well understood, such as dust formation and the incorporation of metals into gas-phase molecules through ion–molecule reactions in these carbon-rich regions. In this study, we present state-to-state collisional cross sections and rate coefficients for the rotational excitation and de-excitation of c-CaC_2 in collisions with He for a wide range of rotational transitions and temperatures ($T \leq 70$ K) relevant to the interstellar medium (ISM). We used *ab initio* high-level CCSD(T)-F12/aug-cc-pVTZ calculations to compute a three-dimensional potential energy surface (3D-PES) for the c-CaC_2–He van der Waals complex. Close-coupling calculations were performed using the analytical potential to determine cross sections for rotational transitions of c-CaC_2 by He collisions, up to 400 cm^{-1}. These cross sections were then thermally averaged to obtain inelastic collision rate coefficients. Our results show that rotational de-excitation with $\Delta j = \Delta k_c = -1$, essential for identifying c-CaC_2 in astronomical surveys, has the highest rate coefficients at temperatures up to 70 K. However, for rotational excitation, transitions with $\Delta j = \Delta k_c = 1$ are dominant only at very low temperatures ($T \leq 10$ K). This work is expected to facilitate the future detection of the metal-carbide CaC_2 in circumstellar and interstellar environments.

P-17: A DECOMPOSITION OF INTERACTION ENERGIES IN PERIODIC MODELS AND ITS INSIGHTS INTO BONDING AND DESCRIPTORS

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We discuss the use of a density-based energy decomposition analysis (EDA) scheme for partitioning interaction energies computed in periodic chemical systems. The method is closely related to a previously applied density-based scheme (dEDA)[1], and it further takes advantage of plane-wave codes that make use of the projector augmented wave (PAW) approach[2] to treat the behaviors of electron orbitals near the atomic nuclei. Like dEDA, it functions by generating a promolecule whose valence electron density reproduces the same valence electron density as the superposition of the underlying fragments. Such schemes classically include terms that account for electrostatic interactions and Pauli repulsion between fragments, as well as the effects of polarization and charge transfer within and between fragments; the particulars of this scheme lead to a different breakdown of the interaction energy but between steps the electron density generally shifts smoothly through and/or near the fragment boundaries. Its simplicity complements well other EDA schemes especially when it is used to compare two or more chemically related systems. It also, importantly, allows for the construction of two-state “Δ-functions” not only from the electron density (i.e., $\Delta\rho$’s) but also from the likes of the electrostatic potential[3, 4] and the electron localization function.

[1] Q. Wu, P. Ayers, and Y. Zhang, J. Chem. Phys., 131 (2009), 164112.

[2] G. Kresse and D. Joubert, Phys. Rev. B, 59 (1999), 1758.

[3] E. Kuzniak-Glanowska et. al., Dalton Trans., 50 (2021), 170.

[4] O. Zurowska and A. Michalak, J. Mol. Modelling, 31 (2025), 33.

P-18: Exploring Excited Molecular States via Localized Orbital Locator: A Quantum Topology Analysis of Charge Transfer in the Ethylene–Tetrafluoroethylene Complex

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In this work, we investigate the charge transfer (CT) excited state of the ethylene (C_2H_4) – tetrafluoroethylene (C_2F_4) complex as a model system using quantum chemical topology (QCT) methods. Our focus is on applying the Quantum Theory of Atoms in Molecules (QTAIM)[1] to excited-state densities in order to understand fundamental changes in the electronic structure upon excitation. Excited-state calculations were performed using TDDFT[2] with the CAM-B3LYP[3] functional. The one-electron transition density matrix was used to derive Natural Transition Orbitals (NTOs), analyzed within a fragment-based electron–hole framework. In parallel, the one-electron reduced density matrix corresponding to the excited state was used to compute the Localized Orbital Locator (LOL)[4], allowing a real-space topological analysis of the excitation. This dual approach enabled a direct comparison between orbital-based and density-based pictures of the excitation, revealing characteristic changes in bond character, lone pair structure, and long-range delocalization patterns induced by charge transfer. These findings demonstrate that topological analysis using LOL and QTAIM can provide valuable insight into the nature of excited states, particularly in identifying subtle but significant electronic rearrangements. Our approach highlights the potential of QCT methods in the study of electronically excited molecules beyond the traditional ground-state domain. Figure 1 illustrates the changes in the Localized Orbital Locator (LOL) contours upon charge transfer from C_2F_4 to C_2H_4. The plots reveal how electron localization is altered in the excited state, particularly highlighting the accumulation of the transferred electron density around the (C_2F_4) fragment.

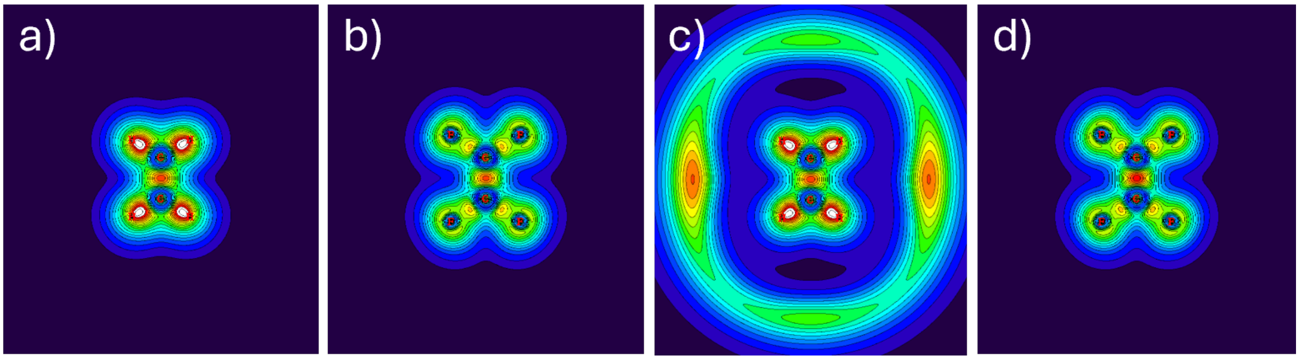

Figure 1: Localized Orbital Locator (LOL) contour plots for (a) ground state of (C_2H_4) ethylene, (b) ground state of (C_2F_4), and (c, d) the respective (CT) excited states.

[1] R. F. W. Bader. Atoms in Molecules: A Quantum Theory. Oxford University Press (1990).

[2] E. Runge, and E. K. U.Gross. Physical Review Letters, 52 (1984) 997–1000.

[3] T. Yanai, D. P. Tew, and N. C. Handy. Chemical Physics Letters, 393 (2004) 51–57.

[4] H.L. Schmider and A.D. Becke. Journal of Molecular Structure: THEOCHEM, 527 (2000) 51-61.

P-19: SELECTED EXCITED-STATE ROVIBRATIONAL AND ELECTRONIC STRUCTURES OF THE CARBON MONOXIDE MOLECULE (PRELIMINARY RESULT)

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Carbon monoxide (CO), the second most abundant molecule in the Universe, is a key tracer in astrophysical environments, such as interstellar clouds and planetary atmospheres. Precise data on CO isotopologues aid studies of star and planet formation. CO also serves as a benchmark in spectroscopy due to rich perturbations in its excited states, especially in $^{13}C^{18}O$, and is relevant in both ecological and industrial contexts [1, 2]. In this work, we present the preliminary results of calculations for the potential energy curves (PECs) of the selected electronic states ($1,2^1S^+$, $1,2^1P$, $1,2^3P$, and $1,2^5P$) of the CO molecule. All PECs were obtained using the complete active space self-consistent field (CASSCF) method, followed by a multireference configuration interaction (MRCI) approach with Davidson correction. We also carefully chose and optimised computational basis sets, similarly to the approach presented in our previous papers [3, 4]. We also calculated the spin-orbit couplings (SOCs) between selected excited states of CO and show their influence on the rovibrational structure manifested in the values of the J-dependent vibrational overlap integrals.

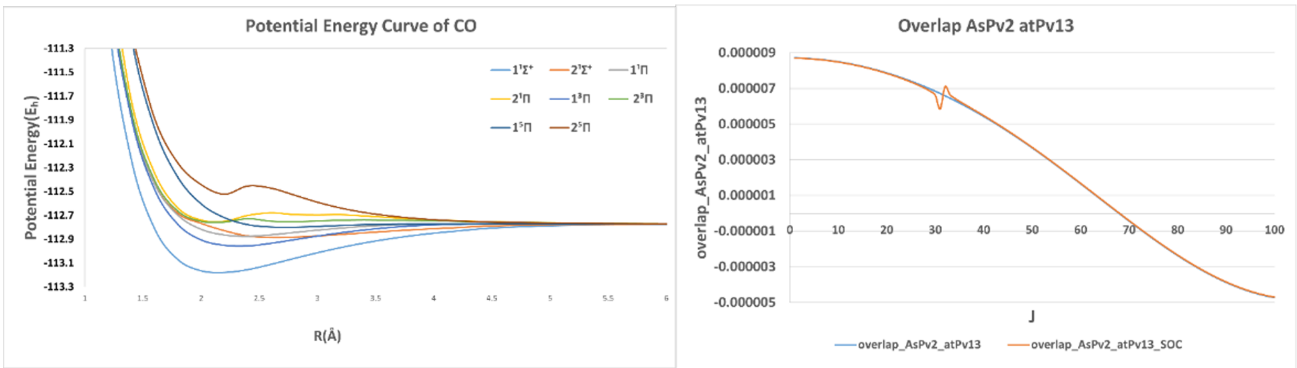

Figure 1: (left panel) The selected PECs of the CO molecule. (right panel) The comparison of the J-dependent vibrational overlap integrals with and without SOCs. We plan to extend these calculations to study interactions of CO molecules with other atoms or molecules in the presence of light, aiming to explore photoinduced effects in such systems.

[1] S. Ryzner, M. I. Malicka, A. N. Heays, R. W. Field, N. de Oliveira, W. Szajna, W. Ubachs, R. Hakalla, J. Mol. Spectrosc., 379 (2021) 111528.

[2] M. I. Malicka, S. Ryzner, A. N. Heays, N. de Oliveira, R. W. Field, W. Ubachs, R. Hakalla, J. Quant. Spectrosc. Radiat. Transf., 247 (2020) 106939.

[3] K. Bączek, P. Jasik, T. Kilich, J. E. Sienkiewicz, Mol. Phys., 120 (2022) 19.

[4] P. Jasik, P. Łobacz, J. E. Sienkiewicz, At. Data Nucl. Data Tables, 149 (2023) 101558.

P-20: MOLECULAR-DYNAMICS ASSISTED MODELING OF FLUORESCENCE DECAY IN MR-TADF EMITTERS

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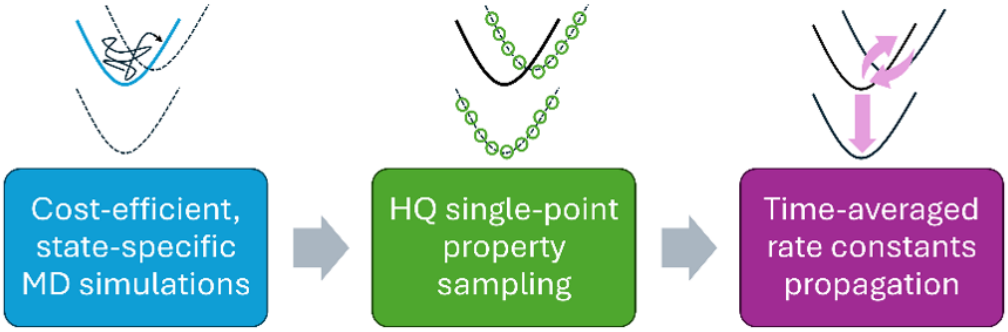
Multiresonance thermally activated delayed fluorescence (MR-TADF) emitters have attracted significant attention due to their ability to achieve near-zero or even negative singlet–triplet energy gaps while maintaining strong emission, enabling efficient reverse and direct intersystem crossing without compromising fluorescence performance. This property is particularly valuable for the development of next-generation energy-efficient OLED materials, as it allows for full harvesting of both singlet and triplet excitons, significantly improving device efficiency without the need for heavy-metal-based phosphors [1].

Given the complexity of the working mechanism standing behind the attractive MR-TADF properties, delivering its accurate theoretical description poses an important, yet challenging goal [2]. In this contribution we will introduce a molecular-dynamics assisted protocol for modeling photodynamics of the MR-TADF emitters, with special focus set on their fluorescence decay [3]. Our model merges advantages of quantum-classical molecular dynamics, which naturally incorporates the finite-temperature vibrational effects beyond the harmonic-oscillator approximation, with cost-efficient and straightforward performance of the well-known kinetic models.



Cost-efficient, state-specific MD simulations

HQ single-point property sampling

Time-averaged rate constants propagation

Figure 1: Workflow scheme of the proposed molecular-dynamics assisted protocol for modeling photodynamics of the MR-TADF emitters.

[1] X. Wu, S. Ni, Ch.-H. Wang, W. Zhu, and P.-T. Chou, Chem. Rev., Article ASAP, DOI: 10.1021/acs.chemrev.5c00021.

[2] M. T. do Casal, Y. Badawy, and D. Escudero, J. Phys. Chem. C, 128 (2024), 18170.

[3] Manuscript in preparation.

P-21: DFT STUDIES ON CU SINGLE ATOM AND SUB-NANOMETER COPPER CLUSTERS DEPOSITED ON TIO$_2$ FOR H$_2$ GENERATION

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The growing interest in materials composed of copper single atoms and/or their sub-nanometric clusters deposited on titania for photo- electrocatalytic H_2 generation prompted us to perform the systematic DFT studies (PBE+D3/def2-TZVP) on systems comprising the anatase phase of titania with Cu_n particles (n= 1 – 7) [1] and Cu-containing MOF (H-KUST-1). The ground-state geometries are proposed and compared with EXAFS data. Cu atoms prefer to aggregate and form larger clusters on TiO_2, as seen from the nucleation energies. The materials are then characterised with the following electronic properties: electronic band structure, natural population charges, frontier orbitals, the H binding energies and the possible H_2 generation mechanism on Cu-MOF/TiO_2. The Cu phase is oxidised once deposited on titania. The charge distribution indicates that the atoms which are the closest to the Cu/TiO_2 interface become the active sites for catalytic processes; Cu atoms are electrophilic while oxygen atoms are nucleophilic. Next, the preferred binding sites for hydrogen atoms are determined. Hydrogen tends to bind with two or three atoms of the hybrid materials, usually copper at the interface with TiO_2, but the H-Ti bonds are found in systems with Cu_1 and Cu_7 clusters too. Among the studied clusters, those containing 1, 4, and 7 Cu atoms exhibit moderate Gibbs free H binding energies indicating them as the best candidates for H_2 evolution.

Our findings are compared with activity of the composite H-KUST-1/TiO_2 in H_2 generation by photocatalysis using H_2O and CH_3OH as sacrificial agent [2]. The calculations for Cu-MOF/TiO_2 show the formation of H_2 on copper sites accompanied by Cu reduction occurring along the H_2 generation in agreement with experiment. They also explain the subtle changes in Cu-bound ligands in Cu-MOF observed by FTIR.

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[1] D. Rutkowska-Zbik, V. Kaipanchery, R. Tokarz-Sobieraj, Catalysis Today, 2025, 446(9), 115142.

[2] A. Khan, et al., Adv. Funct. Mater. 2025, 2501736.

P-22: NONCOVALENT INTERACTIONS IN DENSITY FUNCTIONAL THEORY: ALL THE CHARGE DENSITY WE DO NOT SEE

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Accurate determination of the electron density in molecules and materials enables direct access to interatomic forces via the Hellmann-Feynman theorem. However, density-functional approximations (DFAs) – the workhorse methods for electronic structure – often yield approximate densities that can be unreliable [1, 2, 3]. Here, we show that long-range van der Waals (vdW) dispersion interactions can significantly alter the electron density, exhibiting nontrivial scaling with system size and, in some cases, inducing polarization that exceeds that of the underlying semi-local DFA. To capture these effects, we introduce the Fully-Coupled and Optimally-Tuned Many-Body Dispersion (MBD@FCO) model, which computes the vdW-induced density by appropriately projecting to real space the collective fluctuations of coupled harmonic oscillators. We benchmark our method against accurate coupled-cluster singles and doubles (CCSD) densities for small molecules and extend its application to larger systems, including the S12L [4] and L7 [5] complexes and the Fip35-WW protein. Our findings underscore the potential limitations of post-hoc vdW corrections, highlight the significance of accurately resolving vdW-induced density changes in large (bio)molecules, and pave the way towards improved DFAs and density-based machine-learned force fields.

[1] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, and K. A. Lyssenko, Science, 355 (2017), 49-52.

[2] E. Sim, S. Song, S. Vuckovic, and K. Burke, J. Am. Chem. Soc., 144 (2022), 6625-6639.

[3] N. Ferri, R. A. DiStasio, A. Ambrosetti, R. Car, and A. Tkatchenko, Phys. Rev. Lett., 114 (2015), 176802.

[4] S. Grimme, Chem. Eur. J., 18 (2015), 9955-9964.

[5] R. Sedlak, T. Janowski, M. Pitoňák. J. Řezáč, P. Pulay, and P. Hobza, J. Chem. Theory Comput., 9 (2013), 3364-3374.

P-23: ULTRACOLD HIGHLY POLAR KAg AND CsAg MOLECULES: ELECTRONIC STRUCTURE AND OPTICAL FORMATION

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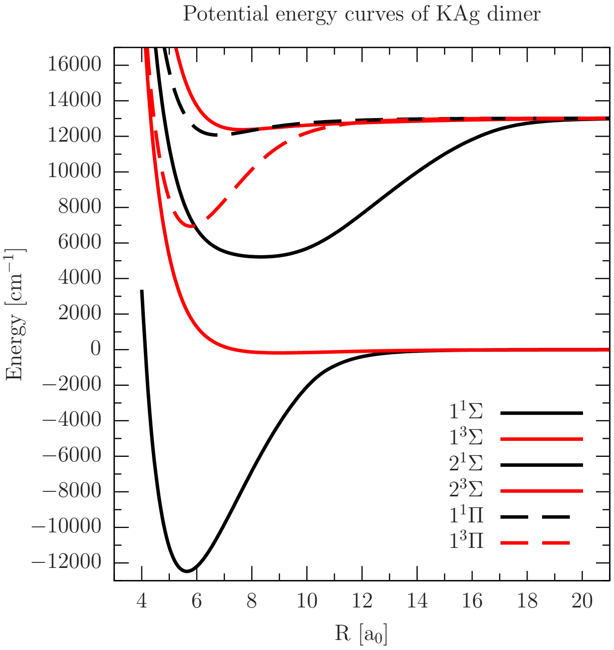
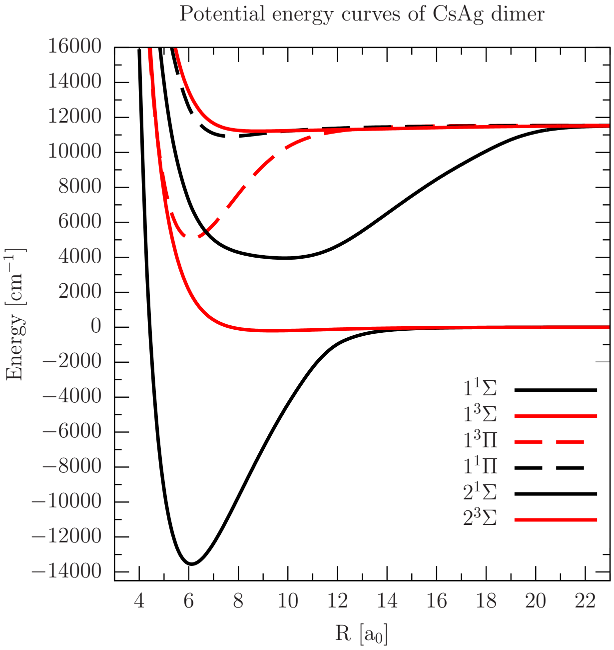
Diatomic molecules consisting of silver and alkali-metal atoms are predicted to possess very large permanent electric dipole moments, approaching 10 debye [1]. In this study, we theoretically investigate the prospects for the formation of ultracold, highly polar KAg and CsAg molecules from ultracold atomic mixtures using photoassociation or magnetoassociation techniques followed by optical stabilization. We calculate the potential energy curves for the first two lowest $^{1,3}\Sigma$ and lowest $^{1,3}\Pi$ states together with the permanent and transition electric dipole moments for the ground and excited electronic states alongside the permanent and transition electric dipole moments for the ground and excited electronic states, employing coupled cluster and multireference configuration interaction methods with large basis sets. Additionally, we determine spin-orbit couplings between these states.





Using the calculated electronic structure data, we calculate vibrational levels, Franck-Condon factors, Einstein coefficients, and radiative lifetimes. We also explore potential pathways for the Stimulated Raman Adiabatic Passage (STIRAP) to transfer weakly bound Feshbach molecules to the absolute ground state. Finally, we assess the experimental feasibility of our proposed approaches.

[1] M. Śmiałkowski, M. Tomza, Phys. Rev. A 103, 022802 (2021).

P-24: PREDICTING MOLECULAR EXCITATIONS INDUCED BY A HIGH-VELOCITY MASSIVE CHARGED PARTICLE

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The objective of the research was to develop a quantum chemical method that enables modeling of interactions between massive high-velocity charged particles and an arbitrary molecule. The proposed method finds broad application across various fields of science. In the context of radiotherapy, a tool capable of accurately describing excitations induced by protons is highly desired to calculate the rate of energy transfer from high-velocity nuclei to tissues [1]. Simultaneously, the ability to predict transition probabilities between molecular electronic states induced by massive charged particles can significantly contribute to the development of high-energy physics, particularly in the search for particles that could potentially constitute dark matter [2]. This study is focused on the second of the aforementioned applications. Two alternative approaches to modeling the interaction between a particle and a molecule were presented, both based on the time-dependent perturbation theory formalism. The massive, charged particle was treated as a classical point particle generating the standard Coulomb potential. The main focus was placed on molecular excitations, neglecting processes such as ionization or electron capture. Excitation probabilities were calculated for water molecules, LAB (linear alkylbenzene) molecules, and argon atoms, induced by a hypothetical dark matter particle (gravitino). Two possible velocities were studied, corresponding to a gravitino bound to the Solar System or the Milky Way Galaxy. Excitation cross sections and characteristic times between excitations were presented for both of them. The results enable the prediction of the gravitino's signature in liquid scintillator detectors. Moreover, it was demonstrated that detectors containing LAB are the most suitable for conducting this type of experiment [3].

[1] M. Grigalavicius, M., Mastrangelopoulou, et al., Nat. Commun. 2019, 10, 3986.

[2] K. A. Meissner and H. Nicolai, J. Cosmol. Astropart. Phys. 2019, 041.

[3] A. Kruk, M. Lesiuk, K.A. Meissner, H. Nicolai, Signatures of supermassive charged gravitinos in liquid scintillator detectors, 2024, in press, accepted in Phys.Rev.Res.

P-25: SELF-CONSISTENT-FIELD SOLUTION FOR UNSTABLE ANIONS

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When using a diffuse basis set to study unstable or temporary anions, the SCF solution often collapses into a minimum energy solution with an extra electron in the most diffuse MO present in the basis set. If more diffuse functions are added to the basis set, the SCF solution for the corresponding unstable anion ultimately converges into a neutral molecule and a free electron. This is known as variational collapse. Therefore, the SCF solution should not be trusted for further use.

The modified PEM is implemented in conjunction with the nuclear charge stabilization method to obtain a meaningful SCF solution for an unstable anion with an extra electron in the valence framework rather than being present in the diffuse MO[1]. Additionally, the continuum states due to which the variational collapse is happening can be removed by modifying Fock matrix and issue of the extra electron being in most diffuse state can be omitted from SCF solution itself. The obtained SCF solution, which avoids the variational collapse, may now be used in post-SCF calculation to account for electron correlation.

[1] Kumar, D.; and Gupta, A.K. ; Phys. Rev. A, 2024, 110, 062821.

P-27: RADIOACTIVE RAAG$^+$ MOLECULAR ION: ELECTRONIC STRUCTURE, FORMATION SCHEMES, AND PROSPECTS FOR PRECISION MEASUREMENTS

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We present a theoretical investigation of the formation of the radioactive molecular ion RaAg$^+$. As a basis for comparison, we first conducted a systematic study of the electronic structure of the $X^1\Sigma$ ground state of radium-alkali-metal molecular ions, RaAlk$^+$ (Alk = Li, Na, K, Rb, Cs and Ag). The ground-state potential energy curves and permanent dipole moments (PDMs) are computed using high-level quantum chemistry methods, specifically the coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)], in combination with large Gaussian basis sets and small-core relativistic energy-consistent pseudopotentials. Subsequently, we determined the excited state potential energy curves and dipole moments of eight λ–S states and fourteen Ω states for RaAg$^+$ using the multireference configuration interaction method with Davidson correction (MRCI+Q). The spectroscopic parameters of the bound states are extracted, and spin-orbit coupling effects are explicitly accounted for in our calculations. Additionally, we employed coupled-channel calculations to estimate the nearest-neighbor density of magnetic-field-induced Feshbach resonances in ultracold Ra$^+$ + Ag collision systems. The present results may be useful for creating a quantum simulator using ultracold Ra$^+$ ions and Ag atoms.

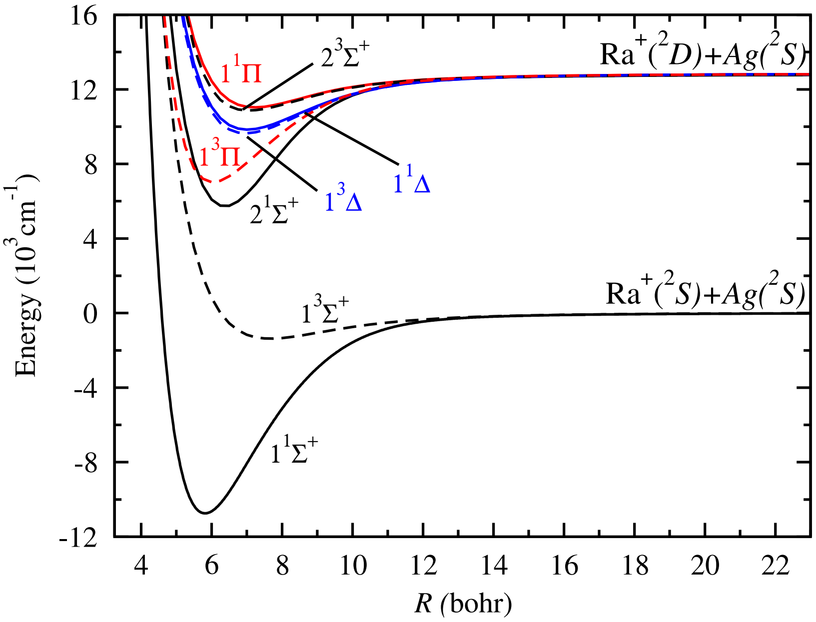

Figure 1: Potential energy curves for the ground and exited states using MRCI+Q and aug-cc-pwCV5Z.

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P-28: THIRD VIRIAL COEFFICIENTS OF HELIUM GAS

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We developed highly accurate ab initio three-body surfaces for the interatomic potential [1], electric polarizability [2] and electric dipole moment [3] of three interacting helium atoms. These surfaces were used to compute the third density and acoustic virial coefficients C, γ_a, and third dielectric virial coefficient C_ϵ. The new interaction potential contains an improved nonrelativistic Born–Oppenheimer energy, nuclear-motion corrections, the leading relativistic together and the retardation effects. Furthermore, interaction potential and polarizability surfaces incorporate two separate fragmentation channels (three-atoms and atom-diatom).

Our results for C and γ_a coefficients agree with previously published calculations, while new estimation of C_ϵ differs from the data computed using an approximated form for the three-body polarizability above 20 K. We also extended to the low-temperature regime by including exchange effects.

In addition, the uncertainties of C, γ_a and C_ϵ is rigorously determined for the first time by propagating the uncertainties of the potential, polarizability and dipole moment surfaces. In the case of interatomic potential, its uncertainty was lowered by 3-5 times in comparison to previous calculations, and no uncertainty estimation was previously published for dielectric or dipole moment surface.

Our results compare reasonably well with the limited experimental data. The first-principles values of the third virial coefficients of helium gas computed in this work will enhance the accuracy of primary temperature and pressure metrology based on measurements of the dielectric constant of helium.

[1] J.Lang, M. Przybytek, M. Lesiuk and B. Jeziorski, J. Chem. Phys., 158 (2023) 114303.

[2] J.Lang, G. Garberoglio, M. Przybytek, M. Jeziorska and B. Jeziorski , Phys. Chem. Chem. Phys., 25 (2023), 23395.

[3] G. Garberoglio, A. H. Harvey, J. Lang, M. Przybytek, M. Lesiuk, B Jeziorski, J. Chem. Phys., 161 (2024), 144111.

NEW CHALLENGES FOR AB INITIO THEORY IN MOLECULAR SCIENCE

POSTER SESSION II

P-29: LONG-RANGE INTERMOLECULAR INTERACTIONS INVOLVING EXCITED STATES OF BENZENE

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Understanding interactions between aromatic molecules has fascinated scientists for a long time [1, 2]. Still, new questions continue to arise, particularly in view of the research and development of organic solar cells [3]. Intermolecular interactions are often computed with density functional theory (DFT) methods and a corresponding dispersion energy correction. But dispersion corrections so far usually do not differentiate between the dispersion of the ground state and that of different excited states [4]. We aim to determine whether this actually makes a significant difference in the dispersion interactions or not. Here, we focus on the dispersion contribution of different excited states in the sandwich configuration of the the benzene dimer. While there is knowledge on singlet excitations in the benzene dimer [5], we concentrate on the interactions between two triplet excited states, which do not seem to be investigated so far. We performed calculations of doubly excited benzene dimers with Complete Active Space Self Consistent Field (CASSCF), followed by N-Electron Valence state Perturbation Theory of 2nd order (NEVPT2). This allowed us to to describe the different intermolecular interactions as a function of distance between the molecules. By removing quadrupole-quadrupole and quadrupole-hexadecapole interactions of the benzene monomers, we found that there are indeed significant differences in the dispersion interaction, introduced by different excited states in the benzene dimer. In future work the dispersion interactions in excited states of the chlorobenzene dimer will be considered.

[1] D. B. Ninković et al., ACS Central Science, 6 (2020), 420-425.
[2] C. A. Hunter and J. K. M. Sanders, Journal of the American Chemical Society, 112 (1990), 5525-5534.
[3] Q. Adfar et al., New Journal of Chemistry, 49 (2025), 2511-2650.
[4] S. Grimme, Computational Molecular Science, 1 (2011), 211-228.
[5] T. Rocha-Rinza et al., Chemical Physics Letters, 426 (2006), 268-272.

P-30: IS THE DEVELOPMENT OF QUANTUM MODELING METHODS SUBJECT TO THE LAWS OF EVOLUTION?

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Objects, phenomena, and processes in the field of natural sciences are described by creating mathematical and computer models, which are then simulated. The agreement of simulation results with experimental observations allows for their temporary acceptance, while the lack of agreement allows for their rejection or at least limitation of their applicability. Based on accepted and rejected models, the next, more accurate, and/or more general generations are then created. This resembles Darwin's evolutionary selection mechanism known from biology. Let us suppose that we limit ourselves to the analysis of intermolecular interactions. One can formulate the question of whether the development of quantum methods of modeling intermolecular interactions is subject to evolutionary laws. Here's the simplified genealogical diagram of quantum intermolecular interaction theories with B. Jeziorski's contributions indicated:

```
                          [Schrödinger Equation]
                           / \
                          /   \
                         /     \
        [Rayleigh-Schrödinger PT]    [Hartree-Fock Theory]
          (1926-1928)               (1930)
                 \                     / \
                  \                   /   \
                   \                 /     \
            [Symmetry-Adapted PT (SAPT)]   [Supermolecular Methods]
             *Jeziorski et al. (1994)*     (HF → MP2 → CCSD(T))
                    / \                     |
                   /   \                    |
                  /     \                   |
   [SAPT(DFT)]           [Effective Fragment Potential]
*Jeziorski et al. (2005)*  *Gordon/Jeziorski (2001)*
                 |                         |
                 |                         |
       [Modern SAPT Variants]       [QM/MM Methods]
       (SAPT(CCSD), SAPT(MBPT))      (1980s-present)

                 [Density Functional Theory]
                          (1965)
                            |
                            |
                   [DFT+vdW Corrections]
                  (DFT-D2/D3, vdW-DF)
                            |
                            |
                 [Many-Body Dispersion]
                   (DFT+MBD, 2012)
```

Analyzing the development of models and theories of quantum-classical molecular dynamics, or especially quantum gravity, yields more extensive evolutionary trees. In the presented research, ChatGPT [1] and DeepSeek [2] were used.

Support, Division of Biophysics, Faculty of Physics, 501-D111-01-1110102.

[1] Q. Liu et al., Innovative Higher Education (2025) https://doi.org/10.1007/s10755-025-09790-4.

[2] A. Liu et al., DeepSeek-V3 Technical Report (2024) ArXiv. https://arxiv.org/abs/2412.19437.

P-31: GREEN'S FUNCTION INTEGRALS WITH SPHERICAL GAUSSIAN AND PLANE-WAVE-MODULATED BASIS FUNCTIONS

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Efficient evaluation of free particle Green's function integrals is essential for *ab initio* quantum mechanical and many-body studies targeting computation of scattering amplitudes and correlation functions [1, 2]. Previous approaches to derive the free particle Green's function integrals were based on Cartesian Gaussian-type orbitals (CGTOs), which are highly inefficient for higher angular momenta. Here we introduce a generalized analytical operator-based framework based on real spherical Gaussian-type orbitals (SGTOs), which naturally includes the angular symmetry for more compact and computationally efficient integral evaluations.

Present operator-based formulation allows the systematic derivation of various molecular integrals by modifying only operator-specific terms. To validate our approach, SGTO-based kinetic energy integrals are benchmarked against Q-Chem data [3]. These results are extended to Green's function integrals through operator substitution. To improve the description of continuum and Rydberg states, we further extend the basis set to SGTOs modulated by plane-wave (PW-SGTOs), which capture oscillatory behavior and enhance asymptotic accuracy. This unified framework provides an efficient and general methodology for computing free-particle Green's function integrals, advancing quantum scattering and continuum-state calculations.

[1] Greenman L, Lucchese R R and McCurdy C W, Phys. Rev. A, 96 (2017) 052706.

[2] Nestmann B M, Krumbach V and Peyerimhoff S D, Phys. Rev. A, 42 (1990), 5406.

[3] Epifanovsky E et al., J. Chem. Phys, 155 (2021) 084801.

P-32: THEORETICAL INVESTIGATION ON FRAGMENTATION OF DIHYDROPYRAN MOLECULE (C_2H_8O)

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We present our recent studies on the fragmentation mechanism of neutral dihydropyran (DHP, C_5H_8O), a compound of interest due to its bioactive derivatives with potential antitumor and antibacterial properties [1, 2, 3]. Firstly, the molecular structure calculations have been performed on the geometries and ionization potentials at the Hartree–Fock level as well as by using other *ab initio* methods such as Coupled Cluster Singles Doubles and perturbative Triples [CCSD(T)], and second-order Møller–Plesset perturbation theory (MP2), with the standard Pople's and Dunning's basis sets. The ionization energies were also calculated using the computationally attractive Density Functional Theory (DFT); the B3LYP hybrid functional was used to fully optimize all geometries on the energy surface without constraints. To explore fragmentation pathways, we applied the Atom-Centered Density Matrix Propagation (ADMP) method to study molecular dynamics under various internal energy levels (in the eV range), identifying potential dissociation channels. All these computations were conducted using GAUSSIAN [4]. In addition, we performed a quantitative analysis of possible fragments by inspecting electron ionization mass spectra (EI MS) generated using other theoretical approaches, including the Quantum Chemistry Mass Spectrometry Program (QCxMS) [5], deep learning models such as NEIMS [6], and a new predictive model for EI MS that we are currently developing.

Financial support by MD-GAS COST Action and GdanskTech is gratefully acknowledged. The calculations have been performed at the Academic Computer Centre (TASK) in Gdańsk.

[1] Y. P. Sui et al., Molecules, 20 (2015), 17614-17626.
[2] D. A. Ostrov et al. Antimicrob. Agents Chemother., 51 (2007), 3688–3698.
[3] L. MacDonagh et al. Cancer Treat. Rev., 41 (2015), 160–169.
[4] M. J. Frisch et al., Gaussian 16, Gaussian Inc., Wallingford CT (2016).
[5] M. S. Doblies, C. Gräbner, F. Köhler, D. E. P. Vanpoucke, S. Grimme, S. Klaproth, J. Am. Soc. Mass Spectrom., 32 (2021), 1335–1346.
[6] J. M. Fine, P. G. Wenthold, ACS Cent. Sci., 5 (2019), 800–810.

P-33: ROTATIONAL EXCITATION AND DE-EXCITATION OF THE INTERSTELLAR PROPARGYL (H_2CCCH^+) CATION BY COLLISIONS WITH HELIUM ATOMS (C_2H_8O)

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The propargyl cation, H_2CCCH^+, is a crucial hydrocarbon precursor in the chemical evolution of the interstellar medium (ISM). It serves as a key intermediate for understanding ISM hydrocarbon chemistry. This work presents state-to-state collisional rate coefficients for rotational excitation and de-excitation of ortho- and para-H_2CCCH^+ colliding with He at ISM-relevant temperatures ($T \leq 60$ K). We employed a high-level post-Hartree–Fock CCSD(T)-F12/aug-cc-pVTZ method to generate a three-dimensional interaction potential energy surface (3D-PES) for the weakly bound H_2CCCH^+–He complex. The analytical 3D-PES was then used in close-coupling calculations to determine cross sections for rotational excitation and de-excitation of ortho- and para-H_2CCCH^+ by collisions with He for kinetic energies (E_k) up to 300 cm^{-1}. Inelastic collision rate coefficients were subsequently obtained by thermally averaging the cross sections over a Maxwell–Boltzmann distribution of kinetic energies. Our results indicate that at very low temperatures ($T < 15$ K), rotational transitions associated with $\Delta j = \Delta k_c = \pm 1$, which are crucial for the identification of H_2CCCH^+ in astronomical surveys, exhibit the largest cross sections. In contrast, at higher temperatures, transitions with $\Delta j = \Delta k_c = \pm 2$ become more dominant. This data holds significant implications for the determination of the H_2CCCH^+ abundance in the ISM and improves the modeling of interstellar hydrocarbon-chain reaction pathways.

P-34: RANK-REDUCED EQUATION-OF-MOTION COUPLED CLUSTER METHODS WITH TRIPLE EXCITATIONS

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Accurate determination of electronic excitation energies is of great importance in, e.g. photochemistry and related fields. Among the single-reference methods, one of the most popular approaches for such calculations is based on the equation-of-motion coupled cluster theory. In particular, EOM-CC3 [1, 2, 3] and EOM-CCSDT [4, 5, 6] methods are known to be very accurate for singly-excited states [7, 8]. Unfortunately, the utility of these methods is hindered by their steep scaling with the system size as well as large memory requirements - both of which originate from the inclusion of triply-excited amplitudes. We present the rank-reduced versions of these methods in which the Tucker decomposition scheme [9] is applied to the triply-excited amplitudes to alleviate the aforementioned problems. Formally, both RR-EOM-CC3 [10] and RR-EOM-CCSDT methods scale as the sixth power of the system size while their parent methods possess the seventh and eighth power scaling, respectively. Moreover, the utilized decomposition scheme results in significant memory savings. We carried out series of calculations and compared the accuracy of the rank-reduced methods with their canonical counterparts. The results indicate that the rank-reduced approach retains the accuracy of the parent canonical method. Thus, the presented methods successfully extend the applicability of the EOM-CC theory to larger molecular systems in the context of accurate calculations of electronic excitation energies.

[1] O. Christiansen, H. Koch and P. Jørgensen, J. Chem. Phys., 103 (1995), 7429.

[2] H. Koch, et al., J. Chem. Phys., 106 (1997), 1808.

[3] A. C. Paul, R. H. Myhre and H. Koch, J. Chem. Theory Comput., 17 (2021), 117.

[4] J. Noga and R. J. Bartlett, J. Chem. Phys., 86 (1987), 7041.

[5] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett., 152 (1988), 382.

[6] S. A. Kucharski, M. Włoch, M. Musiał and R. J. Bartlett, J. Chem. Phys., 115 (2001), 8263.

[7] P.-F. Loos, et al., J. Chem. Theory Comput., 14 (2018), 4360.

[8] P.-F. Loos, et al., J. Chem. Theory Comput., 16 (2020), 1711.

[9] L. R. Tucker, Psychometrika, 31 (1966), 279.

[10] P. Michalak and M. Lesiuk, J. Chem. Theory Comput., 20 (2024), 8970.

P-35: AB INITIO CALCULATIONS OF FESHBACH RESONANCES IN ULTRACOLD COLLISIONS BETWEEN RB AND ALF

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Recent advances in experimental technologies for cooling and trapping atoms and molecules [1, 2] have brought attention to the importance of reliable theoretical predictions of ultracold collisions and reactions based on state-of-the-art *ab initio* calculations. In particular, calculating magnetic Feshbach resonances is desirable because they play essential roles in the interactions between atoms and molecules. However, *ab initio* prediction of individual resonances is still challenging.

In this study, we perform converged scattering calculations to address the magnetic Feshbach resonances for the ultracold collisions between Rb(^{2}S) and AlF($^1\Sigma^+$), efficiently constructing the coupled-channel equations [3]. The interaction potential between Rb and AlF, as well as the geometry-dependent hyperfine coupling parameters (Fig. 1) are obtained with CCSD(T) and CCSD methods, respectively.

We found that the geometry dependence of the hyperfine coupling parameters in the short range of the collision complex is essential for causing the Feshbach resonances. On the other hand, the resonance positions are primarily determined by the coupling between different rotational states, induced by the significant anisotropy of the interaction potential in the short-range.

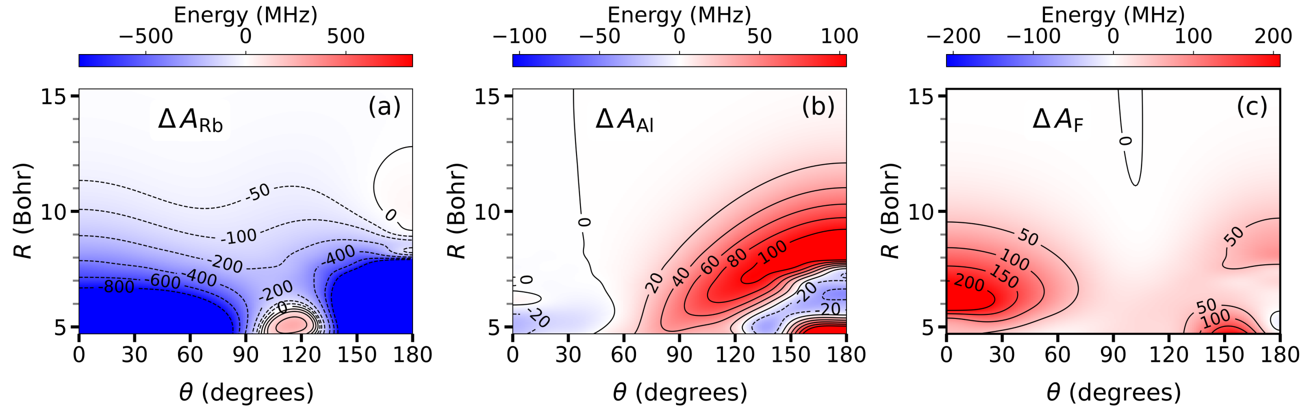

Figure 1: Hyperfine coupling parameter for Rb(^{2}S) and AlF($^1\Sigma^+$). R denotes the distance between Rb and the center of mass of AlF (CM$_{\mathrm{AlF}}$). θ is the angle of Rb-CM$_{\mathrm{AlF}}$-F.

[1] J. L. Bohn, A. M. Rey, and J. Ye, Science 357 (2017) 1002.

[2] T. Karman, M. Tomza, and J. Pérez-Ríos, Nat. Phys., 20 (2024) 722.

[3] T. V. Tscherbul and J. P. D'Incao Phys. Rev. A, 108 (2023) 053317.

P-36: ACCURATE DYNAMIC POLARIZABILITIES IN EXCITED STATES BY MEANS OF ECG BASIS FUNCTIONS

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In recent years, there have been no comprehensive attempts to accurately determine the electrical properties of molecules in their excited states. Historically, however, several publications have addressed small systems in low-lying excited states [1, 2], particularly for few-electron systems such as the helium atom and the hydrogen molecule. Moreover, there are no existing comparisons between highly accurate results and commonly used methods for obtaining response properties [3]. A benchmark study of this kind could be conducted for the beryllium atom in its low-lying excited states using an explicitly correlated Gaussian (ECG) basis set.

The primary research method employed in this study is the use of explicitly correlated Gaussian functions within a variational-perturbative framework. The selected excited states of the beryllium atom are the singlet and triplet 2P states. The results obtained—mainly dynamic and static polarizabilities—are compared with those from the TD-GI method described in [3]. The comparison reveals improvments ranging from 5% to 15% relative to the literature values. For the 3S states, no accurate literature values exist for response properties, making these results the first of their kind.

[1] Chung K. T., Physical Review A, 15 (1977), 1347–134.

[2] Rychlewski J., Komasa J. Cencek W., Physical Review A, 41 (1990), 5825–5833.

[3] TDidier Bégué et al, J. Phys. B: At. Mol. Opt. Phys, 31 (1998), 5077-5084.

P-37: EMBEDDED CLUSTER APPROACH TO DESCRIBE THE ELECTRONIC STRUCTURE OF DOPED CRYSTALS

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Recent developments in the embedded cluster approach, combined with multiconfigurational quantum chemical methods, enable an accurate description of localized electronic states in doped crystalline materials. In this work, we showcase the power of this methodology by investigating two systems of high technological relevance: Th-doped CaF_2 and Pr^{3+}-doped $Sr_3(BO_3)_2$.

For Th:CaF_2, a promising platform for solid-state nuclear clocks [1, 2], we examine how specific defect configurations—particularly fluorine and calcium vacancies—affect the electronic structure and potentially influence non-radiative decay channels near the thorium-229 isomeric transition.

Praseodymium-doped $Sr_3(BO_3)_2$ (SBO:Pr^{3+}) has emerged as a highly efficient ultraviolet C (UVC) upconversion phosphor [3]. Using an embedded cluster approach combined with multiconfigurational quantum chemical calculations (CASSCF/CASPT2), we investigate the electronic structure and excitations responsible for this behavior.

[1] J. Tiedau et al., Phys. Lett. B, 132 (2024), 182501.

[2] K. Nalikowski et al., Phys. Rev. B, 111 (2025), 115103.

[3] P. Zdeb, N. Rebrova, P. Dereń, J. Phys. Chem. Lett. 15 (2024), 9356-9360.

P-38: NON- AND REACTIVE STRUCTURAL EVOLUTION OF INTERMOLECULAR SYSTEMS

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Carbon-carbon bonding mediates countless chemical and biological processes, including structural evolution from simpler to more complex systems. An efficient cross-coupling mechanism via association of bond-terminating counter-ions governs many such reactions. In the 1st part we report its uncommon version with the ions bound noncovalently [1]. We consider formation of a single C-C bond in a halocarbon system, involving an alkali-halide ion-pair. Consistent computations predict a strong (up to 3-fold) decrease of related energy barrier due to counterion constituents. Simulated IR spectra enable tracking the process. The results suggest possible facilitation of such reactions without expensive catalysts (Pd, etc.).

Molecular-system's shape-variations induced by adding/removing an electric charge could enable electronic and/or mechanical functions in molecule-based devices and machines. In the 2nd part we design and characterize a group of binary and ternary complexes of a main-group metalloid atom with hydrocarbon molecules [2]. Their structures differ considerably between neutral and ionic species, and show up to three characteristic conformations associated with the components' relative twisting by up to 90 degrees. Predicted IR spectra enable their experimental detection and tracking of their transformations. The obtained results suggest potential applications of such complexes as molecular switches, with a possibility of monitoring their operation spectroscopically.

[1] S. Kerr and F. Y. Naumkin, Molecules 29 (2024) 4429.

[2] F. Y. Naumkin, Molecules 29 (2024) 1635.

P-39: COMPUTATIONAL STUDIES OF MOLECULAR CRYSTAL EXCITED STATES USING PERIODIC DFT+U CALCULATIONS

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The first goal of this study was to explore the use of the ∆SCF method to investigate the effect of the crystal environment on the phosphorescence of a flat complex of platinum(II) in several supramolecular environments. To achieve it, the PBE+D3+U method was used, in which excited electrons were strategically localized on one of the complexes in the unit cell, which resulted in a quantitatively correct and computationally efficient way to model the emission in fully periodic crystal systems. It was discovered that experimentally determined shifts in the spectrum [1] are successfully reproduced by a periodic model based on GGA. In addition, the red shift resulting from the addition of polyphenol to the crystal structure was attributed to the effect of non-covalent O–H· · ·Pt interaction on the boundary orbitals of the complex, enhanced by the electrostatic potential of the crystal [2].

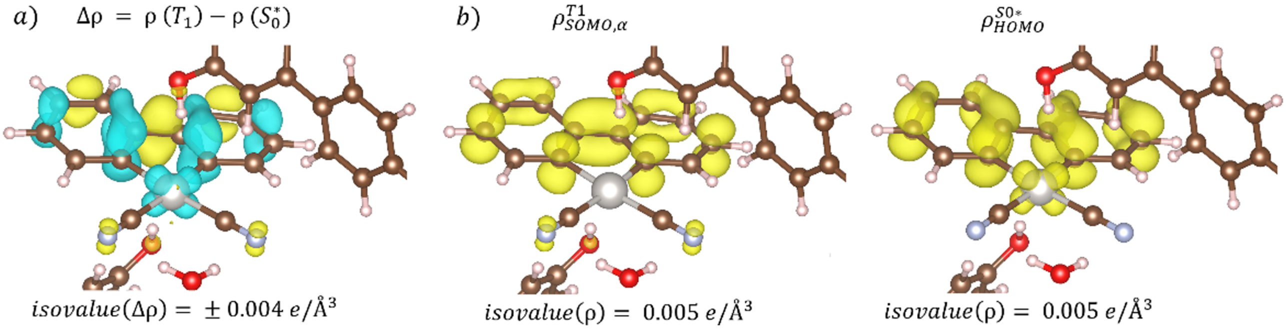

Figure 1: a) Differential electron density between T1 and S0, b) electron density for SOMO and in S0 state on T1 geometry for one of the studied systems.

This study paved a path towards a simple implementation of constrained density functional theory (cDFT) that allows us to break the symmetry of orbitals and localize electronic excitations on one of the symmetry-equivalent molecules in the simulation cell. After successful usage on another photoluminescent system [3], we turned our attention to using such a DFT+U-based ∆SCF method to study absorption as well. Further study on other supramolecular systems revealed the advantages and limitations of such an approach.

[1] C. Wakasugi, M. Yoshida, W. M. C. Sameera, Y. Shigeta, A. Kobayashi, M. Kato, Chem. Eur. J., 26 (2020), 5449.

[2] D. Glosz, K. Jędrzejowska, G. Niedzielski, J. Kobylarczyk, J. J. Zakrzewski, J. G. M. Hooper, M. Gryl, I. O. Koshevoy, R. Podgajny, Chem. Eur. J., 30 (2024), e202400797.

[3] M. Liberka, M. Zychowicz, J. Hooper, K. Nakabayashi, S.-i. Ohkoshi, S. Chorazy, Angew. Chem. Int. Ed., 62 (2023), e202308284.

P-40: ACCURATE AB INITIO CALCULATIONS OF INTERACTION POTENTIALS OF THE ALKALI AND ALKALINE-EARTH METAL HYDRIDES

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Motivation: Simple diatomic molecules play an important role in quantum chemistry and physics by providing the playground for benchmarking molecular theory and implementing quantum control. Precise calculations of molecular properties are crucial for guiding ongoing experiments and for planning new ones. Ultracold molecules provide a good framework for observations of quantum effects and testing various theories. Alkaline-earth metal monohydrides are also promising candidates for a source of ultracold hydrogen [1] and laser cooling to ultralow temperatures [2].

Purpose: Calculations of potential energy curves are a groundwork for determining other molecule properties such as rovibrational states. Neutral alkali and alkaline-earth hydrides have already been extensively studied by others, unlike their ions. Experimental studies on the BaH^{2+} molecule are currently underway in Prof. F. Merkt's group at ETH Zurich. Recently an article about BaH^{+} was published [3]. We aim to provide the interaction energy as accurately as possible using various methods and basis sets.

Methods: We applied coupled cluster theory for post-Hartree-Fock calculations. A range of different electronic structure-describing techniques was employed to achieve a high level of accuracy and provide insightful comparisons. Basis sets with cardinal numbers up to 5Z were utilized and the energies were extrapolated to the complete basis set limit. We applied corrections such as the diagonal Born-Oppenheimer correction (DBOC) and the correction for the full triple excitations in the coupled cluster calculations.

Results: Potential energy curves were calculated for distances ranging from 2 a_0 up to 50 a_0. Adopted corrections helped us improve the accuracy of our results. Additionally, the DBOC correction was also calculated for other alkaline earth metal monohydride ions. We reached a theoretical accuracy of around 0.5% - 1.5% at the minimum.

Summary: The results of our calculations are highly accurate and serve as a strong foundation for deriving other molecular parameters. The ionized alkali and alkaline-earth hydrides have not been extensively studied by others in terms of ab initio calculations and our results are among the most accurate available. Additionally, they provide a valuable reference for comparison with experimental data.

[1] I. C. Lane, Phys. Rev A, 92 (2015), 022511.

[2] S. F. Vázquez-Carson et al, New J. Phys., 24 (2022), 083006.

[3] J. R. Schmitz and F. Merkt, Phys. Chem. Chem. Phys., 27 (2025), 1310-1319.

P-41: ACCURACY OF APPROXIMATE METHODS FOR DESCRIBING MANY-BODY CONTRIBUTIONS OF BINDING ENERGIES OF MOLECULAR CRYSTALS

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Reliable prediction of the structure and stability of molecular crystals is essential for exploring their various applications [1]. However, obtaining reliable binding energies for crystals with many atoms can be prohibitively expensive when using highly accurate methods such as coupled-cluster with singles, doubles, and perturbative triples (CCSD(T)). Moreover, the small differences in energy between polymorphs of crystals result in high requirements not only on the accuracy but also on the precision of the numerical set-up. The many-body expansion (MBE) has emerged as a computationally efficient alternative to periodic boundary conditions for computing binding energies of crystals by decomposing the total binding energy into dimer interactions and non-additive higher-order terms [2, 3]. In this study, we first obtain reference CCSD(T) data for many-body contributions to the binding energy of several crystals with different types of interactions. We then use them to assess the accuracy of approximate methods, including random phase approximation (RPA), Møller–Plesset (MP) perturbation theory, and local natural orbital (LNO) CCSD(T) approach, in describing individual contributions and total binding energies of the considered crystals. We find that both RPA with additional corrections based on PBE orbitals and LNO-CCSD(T) outperform MP methods and achieve nearly benchmark accuracy for the 2-body contributions [4]. However, PBE-based RPA methods yield large errors for the non-additive contributions, where HF-based RPA and MP2.5 provide a much more reliable description. Furthermore, the accuracy of the examined methods depends on the type of interactions in the crystals.

[1] G. J. O. Beran, Chem. Rev., 166 (2015), 5567.
[2] K. Rosciszewski, B. Paulus, P. Fulde, H. Stoll, Phys. Rev. B, 60 (1999), 7905-7910.
[3] J. Hofierka, J. Klimes, Electron. Struct., 3 (2021), 034010.
[4] K. N. Pham, M. Modrejewski, J. Klimes, J. Chem. Phys., 160 (2024), 224101.

P-42: RANK-REDUCED COUPLED CLUSTER THEORY FOR ENERGY GRADIENTS

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We introduce a novel method for computing nuclear gradients within the framework of coupled cluster singles and doubles (CCSD) theory, which capitalizes on the low-rank structure of the canonical doubles amplitude tensor. In contrast to the traditional Lagrangian-based approach [1], our formulation is based on the direct differentiation of the CCSD amplitude equations. By leveraging the intrinsic redundancy of the CCSD amplitude space through a truncated singular value decomposition (SVD), the method achieves an efficient implementation that retains the $\mathcal{O}(N^6)$ scaling of canonical CCSD. This low-rank strategy is also extended to the more accurate CCSD(T) method, similarly maintaining computational scaling no worse than that of the corresponding energy calculation. To assess the performance of the proposed scheme, we compare our results against gradient calculations using a finite-difference approach for hydrogen chains of increasing length and a water molecule, demonstrating both accuracy and computational scaling.

[1] J. Gauss, J. F. Stanton and R. J. Bartlett, J. Chem. Phys. 15 August 1991; 95 (4): 2623–2638.

P-43: RESONANCE WIDTHS OF AUTOIONIZING RYDBERG STATES VIA PROJECTION TECHNIQUE COMBINED WITH EOM-CCSD METHOD

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Rydberg excited states with energies above the lowest ionization threshold can decay through autoionization (Fig 1). Electronically, such states are embedded in the ionization continuum and are examples of Feshbach resonances. Here, we consider autoionizing Rydberg states formed by exciting an electron from an inner-valence orbital of a neutral closed-shell system. To obtain an inner valence excited state, which is stable with respect to autoionization, we added a projector to the standard EOM-EE operator and applied it to the neutral system. The final state is a valence-ionized state, which is computed by the standard EOM-IP-CCSD method. The free electron is modeled as a Coulomb wave where the charge of the wave is the effective charge of the ionized core. The resonance phenomena modeled here are based on the Feshbach-Fano approach [1], where the resonance width is obtained through coupling between the initial (quasi-bound) state and the final (continuum, ionized) states.

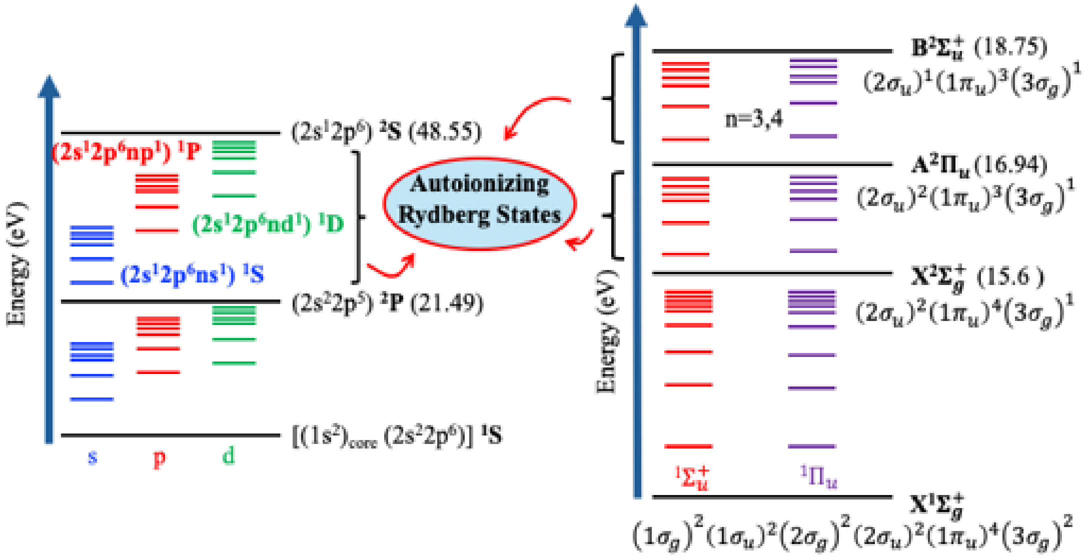

Figure 1: Energy level diagrams of Rydberg series in Ne atom (Left) and N_2 molecule (Right). (adapted from [2].)

We applied our technique to three systems: the Ne atom, the N_2, and the CO_2 molecule. For Neon, we focused on 3s, 3p, 3d, 4s, and 4p Rydberg states, which lie between the first (^2P) and second (^2S) ionization thresholds. For the N_2 molecule, we compute the widths of 3sσ_g, 4sσ_g, 3dσ_g, 4dσ_g ($^1\Sigma_u^+$), and 3dπ_g ($^1\Pi_u$) Rydberg states, which are located between the second ($A^2\Pi_u$) and third ionization ($B^2\Sigma_u^+$) thresholds, corresponding to the Hopfield series. In the case of CO_2, we calculated nsσ_g ($n = 6$–8) and ndσ_g ($n = 5$–7) Rydberg states of $^1\Sigma_u^+$ symmetry (between the second $A^2\Pi_u$ and third $B^2\Sigma_u^+$ ionization potential thresholds), which belong to the Henning diffuse and sharp series. Our methodology provides results consistent with those obtained from other computational techniques, such as complex scaling and complex basis function techniques [2]. Additionally, it is applicable to larger systems.

[1] W. Skomorowski, A. I. Krylov, J. Chem. Phys. 154 (2021).

[2] J. Creutzberg, W. Skomorowski, T. C. Jagau, J. Phys. Chem. Lett. 14 (2023), 10943–10950.

P-44: IMPROVING DOUBLE HYBRID FUNCTIONALS VIA REGULARIZED SECOND-ORDER PERTURBATION THEORY

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Møller-Plesset second-order (MP2) perturbation energy expression has been a workhorse for quantum chemistry methods for many years. It has been widely utilized in the post-Hartree-Fock (post-HF) calculations and Kohn-Sham density functional theory (KS-DFT) to define various classes of functionals, i.e., Double Hybrids (DH). Although the list of successful applications of the MP2 method is quite long, it suffers from many limitations like divergence in the cases where HOMO-LUMO energy gap closes, metallic systems, and large $\pi - \pi$ stacking systems.

Recently we have shown that it is possible to improve MP2 with it's regularized counterparts in context of post-HF and KS-DFT calculations [1]. In this work we focus on one of the regularized methods - Quasi Particle Perturbation Theory [2]. This version of Perturbation Theory is particularly interesting as it ab initio, size extensive and size consistent method. Functionals combined with regularized MP2 are in most cases on par with the standard implementations of DH functionals. In some however, they show an improvement in broad benchmarks ranging from main group thermochemistry to dissociation energies and strong correlation systems [1]. We also present that DH functionals with parameters optimized for MP2 can be significantly improved in terms of Mean Average Errors if one instead optimizes their parameters with 2nd order Quasi Particle Perturbation Theory.

[1] I. Sawicki, V. Triglione, S. Jana and S. Śmiga
Journal of Chemical Theory and Computation, (2025) 21 (6).

[2] Christopher J. N. Coveney and David P. Tew
Journal of Chemical Theory and Computation, (2023) 19 (13).

P-45: ULTRAFAST ELECTRONIC CHIRALITY FLIPS IN THE TRIATOMIC MOLECULE NSF: A NEW APPLICATION OF AB INITIO QUANTUM CHEMISTRY

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State-of-the-art *ab initio* methods of quantum chemistry evaluate properties of molecular electronic eigenstates, e.g. of the ground or excited states, at fixed nuclear geometries. Well-designed ultrashort laser pulses can prepare specific superpositions of these eigenstates, with new properties. These electronic superposition states are no longer eigenstates. Instead, they represent ultrafast electron dynamics on typical time scales from a few hundred attoseconds (as) to a few femtoseconds (fs), when the nuclei stand practically still. Often, these superposition states break the symmetry of the density of the electronic eigenstates. [1, 2] In extreme cases, they even break all symmetry elements. In such cases, ultrashort laser pulses generate chirality in the density of the electronic superposition states, with chirality flips in the as-to-fs time domain, even though the nuclear frames remain achiral. This phenomenon has been demonstrated first for oriented hetero-nuclear diatomic molecules such as NaK. [3] Here we present a new, much simpler application, namely to the oriented bent triatomic molecule, NSF. The resume is that preparation of its $\mathrm{A}' + \mathrm{A}''$ superposition state by a single laser pulse induces electronic chirality flips with period 1.13 fs.

[1] D. Haase, J. Manz, J. C. Tremblay, J. Phys. Chem. A, 124 (2020) 3329.

[2] D. Haase, G. Hermann, J. Manz, V. Pohl, J. C. Tremblay, Symmetry, 13 (2021) 205.

[3] Y. Chen, D. Haase, J. Manz, H. Wang, Y. Yang, Nature Comm., 15 (2024) 565.

P-46: APPLICATION OF SAPT FOR CONSTRUCTING TRANSFERABLE INTERMOLECULAR POTENTIALS

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Symmetry-adapted perturbation theory (SAPT) is an effective tool for calculating the intermolecular interaction energy E_{int} of van der Waals complexes [1]. It is intended to kill two birds with one stone by providing accurate E_{int} values free from basis set superposition error, while also decomposing E_{int} into physically meaningful components such as electrostatics, exchange, induction, and dispersion. The computationally inexpensive version of SAPT, based on density functional theory (DFT-SAPT) [2], is often used to calculate E_{int} and construct analytical potential energy surfaces for complexes where employing accurate *ab initio* supermolecular methods is computationally challenging [3]. The parameters of the constructed potentials must be transferable across a wide range of molecular complexes, eliminating the need for electronic structure calculations of each specific complex while providing near-*ab initio* accuracy. Such potentials can then be used to interpret a wide range of experimental data, including spectroscopic, scattering, and thermochemical measurements.

[1] B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev., 94 (1994), 1887.
[2] G. Jansen, WIREs: Comput. Mol. Sci, 4 (2013), 127.
[3] L. Shirkov and J. Makarewicz and, J. Chem. Phys., 150 (2019), 074302.

P-47: UNIVERSALLY APPLICABLE RANGE-SEPARATION TUNING

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Range-separated hybrid functionals that employ strategies such as "ionization energy" or "optimal tuning" [1, 2] of the screening parameter are widely recognized as effective and precise tools for modeling excited-state behavior in diverse systems, such as condensed phase matter. However, these techniques often require iterative self-consistent computations, which can be computationally demanding and prone to instability, especially in large-scale systems.
This study [3] introduces a straightforward and efficient alternative to determine the screening parameter, relying exclusively on the total electron density of the system and the density functional theory (DFT) compressibility sum rule. The resulting parameter demonstrates exceptional accuracy, particularly for charge-transfer excitations, outperforming the previously proposed methods [4]. By solely relying on the electron density, the approach offers a clear theoretical foundation and is easily adaptable to automated DFT workflows in complex or bulk systems, where conventional tuning strategies are impractical.

[1] Leeor Kronik, Stephan Kümmel, Dielectric Screening Meets Optimally Tuned Density Functionals, DOI: 10.1002/adma.201706560, Advanced Materials, 30(41):e1706560, 2018.

[2] Refaely-Abramson, Sivan and Sharifzadeh, Sahar and Govind, Niranjan and Autschbach, Jochen and Neaton, Jeffrey B. and Baer, Roi and Kronik, Leeor, Quasiparticle Spectra from a Nonempirical Optimally Tuned Range-Separated Hybrid Density Functional, 109, 22, 226405, Phys. Rev. Lett., 2012.

[3] iti Singh, Subrata Jana, Lucian A. Constantin, Fabio Della Sala, Prasanjit Samal, Szymon Śmiga, Simplified, Physically Motivated, and Universally Applicable Range Separation Tuning, arXiv preprint arXiv:2505.08383 (13 May 2025).

[4] Aniket Mandal and John M. Herbert, The Journal of Physical Chemistry Letters, 16, 10, 2672-2680, 2025.

P-48: EXPLORING NON-COVALENT INTERACTIONS IN SUPRAMOLECULAR SYSTEMS USING DENSITY FUNCTIONAL THEORY

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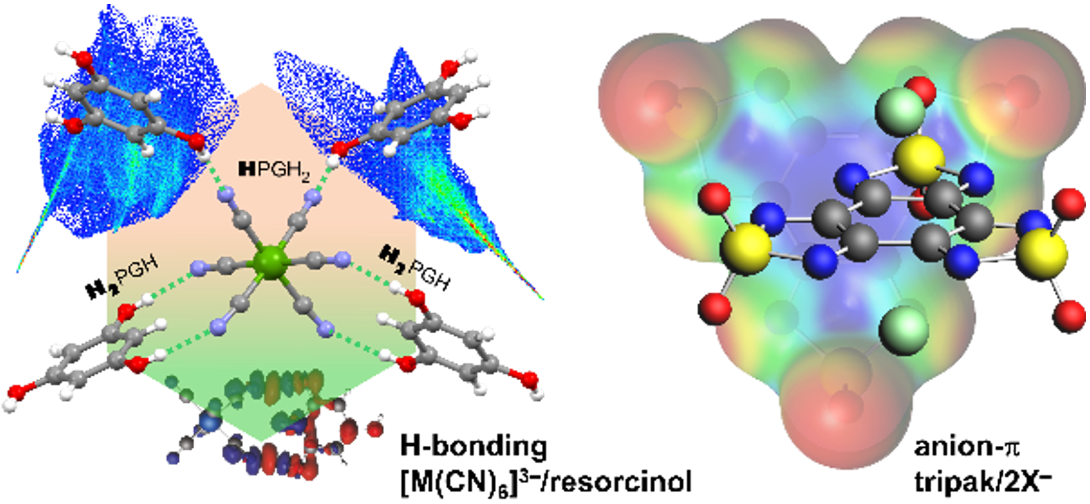
Supramolecular systems—assemblies of chemical subunits organized through intermolecular interactions ranging from covalent to non-covalent—have garnered significant attention for the development of innovative materials and technologies across diverse fields such as materials science, biochemistry, analytical chemistry, and nanomedicine [1]. Quantum-chemical calculations play a crucial role in studying the electronic structure of these systems, as understanding the nature and strength of the underlying interactions is key to elucidating their properties and functions.

Recently, a variety of novel supramolecular architectures have been successfully characterized in our laboratory in collaboration with the experimental teams of the Inorganic Molecular Materials Group at the Faculty of Chemistry, Jagiellonian University. These studies employed density functional theory (DFT) calculations and ETS-NOCV [2] charge and bonding energy decomposition analysis. Representative examples include co-crystal salts stabilized by anion–π interactions (involving both simple and complex anions) and/or hydrogen bonding [3, 4, 5, 6] (see Figure 1). Selected results will be presented in this contribution, with a focus on understanding the factors that govern the nature and strength of intermolecular interactions and their influence on the spectroscopic properties of these assemblies.



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[1] G. T. Williams, C. J. E. Haynes, M. Fares, C. Caltagirone, J. R. Hiscock, and P. A. Gale, Chem. Soc. Rev., 50 (2021), 2737.

[2] M. P. Mitoraj, A. Michalak, and T. Ziegler, J. Chem. Theory Comput., 5 (2009), 962.

[3] E. Kuzniak-Glanowska, D. Glosz, G. Niedzielski, J. Kobylarczyk, M. Srebro-Hooper, J. G. M. Hooper, and R. Podgajny, Dalton Trans., 50 (2021), 170.

[4] K. Jędrzejowska, J. Kobylarczyk, D. Glosz, E. Kuzniak-Glanowska, D. Tabor, M. Srebro-Hooper, J. J. Zakrzewski, K. Dziedzic-Kocurek, T. M. Muzioł, and R. Podgajny, Molecules, 27 (2022), 4111.

[5] K. Jędrzejowska, J. Kobylarczyk, D. Tabor, M. Srebro-Hooper, K. Kumar, G. Li, O. Stefanczyk, T. M. Muzioł, K. Dziedzic-Kocurek, S.-i. Ohkoshi, and R. Podgajny, Inorg. Chem., 63 (2024), 1803.

[6] P. Pakulski, M. Magott, S. Chorazy, M. Sarewicz, M. Srebro-Hooper, D. Tabor, Ł. Łapok, D. Szczepanik, S. Demir, and D. Pinkowicz, Chem, 10 (2024), 971.

P-49: COMPLEX POTENTIAL ENERGY SURFACES FOR PENNING IONIZATION THROUGH COMPLEX BASIS FUNCTIONS

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enning ionization (PI) is a phenomenon where a neutral atom or molecule (say B) is ionized upon approaching another neutral atom in its internally excited metastable state (say A*)—with a sufficiently long lifetime that does not decay through spontaneous emission [1]. It is commonly represented as:

$$\mathrm{A}^* + \mathrm{B} \to \mathrm{A} + \mathrm{B}^+ + e^-. \tag{1}$$

PI occurs when the excitation energy of A* is higher than the ionization potential of B. Energetically, PI is highly exothermic, allowing such collisions to occur even at very low collision energies, within the cold-chemistry regime [2]. During the interaction, an auto-ionizing complex (A*–B) forms, which is categorized as a Feshbach resonance—a subset of electronic resonances [3]. To accurately model these resonances, non-Hermitian quantum chemical methods have been found to be particularly effective [4, 5]. Among the various available approaches, the complex basis functions (CBFs) method is known for its general applicability to molecular resonances. This technique yields complex potential energy surfaces (V) as functions of the interatomic distance (R):

$$V(R) = V_*(R) - i\frac{\Gamma(R)}{2}, \tag{2}$$

where the real part $V_*(R)$ describes the relative dynamics, and the imaginary part $\Gamma(R)$ characterizes the ionization probability and is directly related to the lifetime of the complex ($\tau = 1/\Gamma$). Here, we investigated He*(^{3}S) + Ar, He*(^{3}S) + H, and Ne*(^{3}P$_{0,2}$) + Ar chemical systems using the equation-of-motion coupled-cluster method with single and double excitations (EOM-CCSD) combined with CBFs. We demonstrate that the CBF approach provides a robust framework for modeling PI, despite the considerable computational cost involved. The obtained results are compared with the available experimental data.

[1] M. J. Druyvesteyn and F. M. Penning, Rev. Mod. Phys. 12 (1940), 87.

[2] A. B. Henson *et al.* Science. **2012**, 338 (234).

[3] P. E. Siska, Rev. Mod. Phys. 65 (1993), 337.

[4] N. Moiseyev, *Non-Hermitian Quantum Mechanics*, Cambridge University, (2011).

[5] T. -C. Jagau, Chem. Commun. 58 (2022), 5205.

P-50: MULTI-LEVEL COUPLED-CLUSTER DESCRIPTION OF CRYSTAL LATTICE ENERGIES

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The many-body expansion (MBE) of the lattice energy enables an ab initio description of molecular solids using correlated wave function approximations. However, the practical application of MBE requires computing the large number of n-body contributions efficiently. To this end, we employ a multi-level coupled-cluster approach which adapts the approximation level based on interaction type and intermolecular distance [1]. The high-level method, including connected triple excitations, is applied only to monomer relaxation and dimer interactions roughly within the first and second coordination shells (Fig. 1. Long-range dimers and trimers are treated using a simplified coupled-cluster description based on the random-phase approximation (RPA). A key feature is an energy correction which mitigates the underbinding error of the base RPA. Convergence to the bulk limit is accelerated by the addition of the periodic Hartree–Fock correction. The proposed approach is validated against recent diffusion Monte Carlo reference data for the X23 data set [2], achieving a mean absolute error of 3.1 kJ/mol, i.e., chemical accuracy for absolute lattice energies.

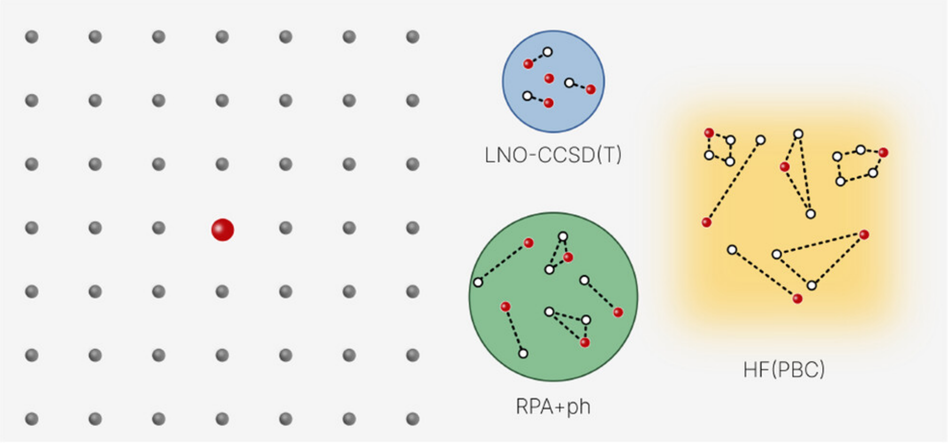

Figure 1: Partitioning of dimer, trimer, and higher-body contributions to the lattice energy into subsets treated with LNO-CCSD(T), RPA+ph, and periodic HF, based on cluster type and intermolecular distance. A transition between levels of theory occurs if any pair of molecules within a cluster is separated by more than the switchover radius.

[1] F. Della Pia et al. Phys. Rev. Lett. 133.4 (2024): 046401.
[2] K. Syty et al. J. Chem. Theory Comput. (2025).

P-51: ENHANCED DMRG-AC APPROACH FOR EFFICIENT TREATMENT OF STRONGLY CORRELATED SYSTEMS

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One of the main challenges of modern quantum chemistry is the description of large, strongly correlated systems. The density matrix renormalization group (DMRG) method handles systems with large active spaces, but does not fully capture dynamic correlation. While multiple post-DMRG methods have been developed to address this problem, they typically have high computational cost due to their reliance on higher-order reduced density matrices (RDMs).
The adiabatic connection (AC) approach, DMRG-AC [1] is a post-DMRG method that utilizes only the 1- and 2-RDMs, significantly reducing computational complexity. Despite its promising results it has notable limitations: overestimation of singlet excitations and neglect of double and higher-order excitations in the extended random phase approximation (ERPA) underlying existing multireference AC methods. To resolve these issues, we propose enhancements to the original DMRG-AC framework.
Recently, we introduced the ffAC [2] method, which rigorously combines multireference particle-hole and particle-particle AC approaches. This combination significantly improves the description of singlet excitations, providing accuracy comparable to or even surpassing NEVPT2. Additionally, to address the limitation of the random phase approximation employed in AC, and increase the overall accuracy of the DMRG-AC method, we propose a further modification that goes beyond ERPA and incorporates essential double excitations while maintaining computational efficiency. Our improved method achieves reduced computational scaling:retaining a favorable, unmatched by perturbation methods, scaling with the 6th power in the number of active orbitals making it particularly suitable for large, strongly correlated systems.

[1] Beran, P., Matoušek, M., Hapka, M., Pernal, K., & Veis, L. (2021). Journal of Chemical Theory and Computation, 17(12), 7575-7585.

[2] Tucholska, A., Guo, Y., & Pernal, K. (2024). J. Phys. Chem. Lett., 15(48), 12001-12009.

P-52: RECENT DEVELOPMENTS IN SECOND-QUANTIZATION-BASED SYMMETRY-ADAPTED PERTURBATION THEORY

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The poster contribution summarizes recent advancements in symmetry-adapted perturbation theory (SAPT) [1, 2, 3] developed by our group and our collaborators. All of the developments are connected through having one thing in common: they are all based on the second quantization formalism [4, 5]. The mentioned advancements include i.a., deriving and implementing first- and second-order exchange energy corrections (namely $E^{(10)}_{\text{exch}}$, $E^{20}_{\text{exch-ind}}$ and $E^{(20)}_{\text{exch-disp}}$) without the so-called *single-exchange* approximation in the second-quantized formalism [6]. This methodology was also extended to the third-order exchange-induction-dispersion energy $E^{(30)}_{\text{exch-ind-disp}}$ to obtain its unapproximated version [7]. Another noteworthy development is the extension of the SAPT capabilities to analytical derivatives for the calculations of interaction-induced properties (e.g., dipole moments) in the approach called propSAPT [8]. The current, most exciting effort is the development of a new SAPT-inspired method of calculating the dispersionless interaction energy through the use of the variational principle. This method called symmetry-adapted relaxation theory [9] (SART), is capable of obtaining the induction energy in the infinite order of the intermolecular interaction operator, accounting at the same time for the proper orbital relaxation effects. Eventually, the development of the code for symbolic derivations of second-quantized SAPT expressions from our group has proven to be highly beneficial in the work towards the mentioned advancements [10].

[1] K. Patkowski, “Recent developments in symmetry-adapted perturbation theory”, en, WIREs Computational Molecular Science 10, e1452 (2020).

[2] K. Szalewicz, “Symmetry-adapted perturbation theory of intermolecular forces”, en, WIREs Computational Molecular Science 2, 254–272 (2012).

[3] B. Jeziorski, R. Moszyński, and K. Szalewicz, “Perturbation Theory Approach to Intermolecular Potential Energy Surfaces of van der Waals Complexes”, Chemical Reviews 94, 1887–1930 (1994).

[4] S. Rybak, B. Jeziorski, and K. Szalewicz, “Many-body symmetry-adapted perturbation theory of intermolecular interactions. H2O and HF dimers”, The Journal of Chemical Physics 95, 6576–6601 (1991).

[5] R. Moszynski, B. Jeziorski, and K. Szalewicz, “Many-body theory of exchange effects in intermolecular interactions. Second-quantization approach and comparison with full configuration interaction results”, The Journal of Chemical Physics 100, 1312–1325 (1994).

[6] B. Tyrcha, F. Brzęk, and P. S. Żuchowski, “Second quantization-based symmetry-adapted perturbation theory: Generalizing exchange beyond single electron pair approximation”, The Journal of Chemical Physics 160, 044118 (2024).

[7] 7B. Tyrcha, P. S. Żuchowski, and K. Patkowski, “Third-order exchange-induction-dispersion energy without single-exchange approximation in symmetry-adapted perturbation theory”, in preparation (unpublished), 2025.

[8] 8B. Tyrcha, T. Gupta, K. Patkowski, and P. S. Żuchowski, “Analytical Derivatives of Symmetry-Adapted Perturbation Theory Corrections for Interaction-Induced Properties”, Journal of Chemical Theory and Computation 21, 4562–4578 (2025).

[9] 9H. Dihingia, E. Vanich, B. Tyrcha, P. S. Żuchowski, and A. J. Misquitta, “Variational calculation of dispersionfree interaction energy”, in preparation (unpublished), 2025.

[10] 10B. Tyrcha, “Automatic implementation of expressions of symmetry-adapted perturbation theory”, Bachelor Thesis (Nicolaus Copernicus University in Toruń, Toruń, 2021).

P-53: COMPARING FULLY SELF-CONSISTENCY GW (SCGW) AND FULLY SELF-CONSISTENCY VERTEX-CORRECTED GW (SCGWΓ) WITH TENSOR HYPERCONTRACTION

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An approximation in the GW method is the omission of the vertex term, Γ, which accounts for higher-order interactions captured by polarizability and self-energy. Previous studies of GWΓ have been limited to G_0W_0 or quasiparticle self-consistent schemes, which remain reference-dependent and can inherit errors from the starting point. In this work, we eliminate that dependency by performing fully self-consistent vertex-corrected GW calculations enabled by tensor hypercontraction (THC) to remove any bias from the initial guess and isolate the true effect of the vertex on quasiparticle energies.

To make these fully self-consistent vertex-corrected GW calculations tractable, we employ THC to decompose the four-index electron repulsion integrals (ERIs) into two-index objects. This decomposition dramatically lowers both memory requirements and computational cost, enabling advanced GW schemes to be applied to larger systems.

We implement and compare a hierarchy of approximations: the second-order exchange (SOX) term and several screened variants (static-SOSEX, static-2SOSEX, static-G3W2, dynamic-SOSEX, dynamic-2SOSEX), considering both fully frequency-dependent and static screening. First ionization potentials are then computed for 29 small molecules [1] and the GW100 test set [2], providing clear benchmarks for the role and limits of vertex corrections in predictive GWΓ calculations.

By including the vertex exclusively in the self-energy, while preserving the original polarizability, we eliminate the confounding influence of modified screening and examine how adding the vertex shifts both absolute energies and relative trends. Our study covers a broad range of molecular systems and reveals that, instead of improving agreement with experimental data, the inclusion of vertex corrections induces a nearly uniform shift in the predicted ionization potentials. This suggests that their primary effect is a global energy offset rather than an enhancement in relative accuracy, as observed in our earlier work [3, 4].

[1] Maggio, E.; Kresse, G. GW Vertex Corrected Calculations for Molecular Systems. J. Chem. Theory Comput. 2017, 13, 4765-4778.

[2] Wang, Y.; Rinke, P.; Ren, X. Assessing the G0W0Γ0(1) Approach: Beyond G0W0 with Hedin's Full Second-Order Self-Energy Contribution. J. Chem. Theory Comput. 2021, 17, 5140-5154.

[3] Pokhilko, P.; Yeh, C. N.; Morales, M. A.; Zgid, D. Tensor Hypercontraction for Fully Self-Consistent Imaginary-Time GF2 and GWSOX Methods: Theory, Implementation, and Role of the Green's Function Second-Order Exchange for Intermolecular Interactions. J. Chem. Phys. 2024, 161, 084108.

[4] Wen, M.; Abraham, V.; Harsha, G.; Shee, A.; Whaley, K. B.; Zgid, D. Comparing Self-Consistent GW and Vertex-Corrected G0W0 (G0W0Γ) Accuracy for Molecular Ionization Potentials. J. Chem. Theory Comput. 2024, 20, 3109-3120.

P-54: APPROXIMATING PAULI EXCHANGE-REPULSION: A TRANSFERRABLE MODEL BASED ON ELECTRON DENSITY

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Current approaches to modeling Pauli repulsion in molecular force fields for biological systems often rely on over 20 atom types to achieve chemical accuracy. The number of parameters in these approaches hampers the development of force fields with quantum-chemical accuracy that are transferrable across many chemical systems, as fitting procedures tend to conflate exchange-repulsion with other short-range effects such as polarization, charge transfer, and dispersion. We present a low-parameter, semi-classical model for exchange-repulsion derived from the electron density. This electrostatics-based model reproduces symmetry-adapted perturbation theory (SAPT) reference energies with chemical accuracy for a representative set of atomic dimers and small organic molecules. Its minimal parameterization and high accuracy presents the possibility of fitting to high-level reference calculations while preserving transferability across chemical systems, offering a promising path toward high-accuracy, next-generation force fields.

P-55: PROGRESS IN EXACT ANALYTIC SOLUTION OF SCHRÖDINGER EQUATION OF THE HELIUM ATOM

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Exact solutions to Schrödinger equation are known but for a few simplest quantum systems. Numerically exact solutions are available for a much larger class of systems, but the associated eigensolutions provide limited and sometimes incorrect insight into the analytical structure of the exact wave functions. The current poster summarizes the 14 years' research activity [1, 2, 3] in our group devoted to unravelling the analytic structure of the exact quantum wave functions for two electrons in a central field aka the helium atom.
Implicit analytical form of the ground state wave function for helium

$$\Psi(r_1,r_2,r_{12}) = \sum_{n=0}^{\infty} \underbrace{\sqrt{{r_1}^2+{r_2}^2}}_{r}{}^{n} \sum_{p=0}^{\left\lfloor \frac{n}{2} \right\rfloor} (\ln({r_1}^2+{r_2}^2))^p \cdot \psi_{np}\left(\underbrace{\frac{{r_1}^2-{r_2}^2}{{r_1}^2+{r_2}^2}}_{\cos\alpha}, \underbrace{\frac{{r_1}^2+{r_2}^2-{r_{12}}^2}{2r_1r_2}}_{\cos\theta}\right)$$

was first proposed by Fock in 1954 [4]. Explicit determination of the angular Fock coefficients $\psi_{np}(\cos\alpha, \cos\theta)$ turned out to be a complex task; only a few of them are known [5] in closed form up to date. The Fock formal solution can be considered as a generalized Taylor series of the exact wave function in the coordinates $(r, \ln r, \cos\alpha, \cos\theta)$ around the triple coalescence point $r = 0$. Our poster summarizes the results obtained in our group using an alternative technique (based on the concept of generalized homogeneity) to solve this problem initiated originally by Hylleraas and developed further by Abbott, Gottschalk, and Maslen. Using this technique, the Fock series emerges naturally. In particular, the logarithmic terms appear in low-order Fock coefficients in order to guarantee physical behavior (continuity and finiteness) of the resulting wave function. These logarithmic terms appear as solutions of ordinary differential equations (ODEs) in cases when the usual Hylleraas recurrence relations become singular. Our up-to-date results constitute only a fraction of work needed to complete the task of determining the exact helium wave function. However, the analytical tools designed in our group are general, and it is only a question of time to find the remaining, yet-unknown analytical components of the exact solution.

[1] W.-Y. Tsai, MS Thesis, NCTU (2014).

[2] J. Langner, PhD Thesis, NYCU (2022).

[3] B.-H. He, H. A. Witek, J. Chin. Chem. Soc. 63 (2016), 69.

[4] V. A. Fock, Norske Vidensk. Selsk. Forh. 31 (1958), 138 [also: Izv. Akad. Nauk 18 (1954), 161].

[5] A. M. Ermolaev, Vest. Len. Univ. 16 (1961), 19; P. C. Abbott, E. N. Maslen, J. Phys. A, 20 (1987), 2043; J. E. Gottschalk, P. C. Abbott, E. N. Maslen, J. Phys. A, 20 (1987), 2077; J. E. Gottschalk, E. N. Maslen, J. Phys. A, 20 (1987), 2781; E. Z. Liverts and N. Barnea, Phys. Rev. A 92 (2015), 042512.

P-56: ULTRAFAST CORRELATION-ENERGY ESTIMATOR

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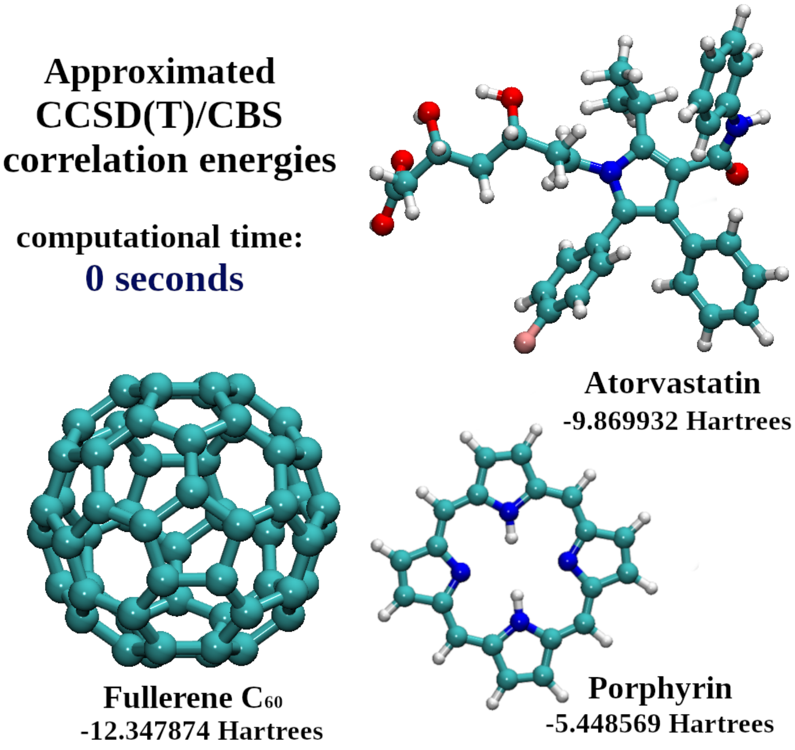
We introduce a novel computational method, Correlation Energy per Bond (CEPB), for efficiently estimating electron correlation energies with CCSD(T)-level accuracy at minimal numerical cost. By partitioning the molecular correlation energy into contributions from individual chemical bonds, the method is not size limited and can be applied to even large molecules, including proteins. Once these bond-specific energies are determined from independent calculations, they can be utilized across different molecular systems, making the approach both scalable and transferable. We demonstrated the effectiveness of the method on systems containing up to 650 atoms, showing highly accurate correlation energy predictions. Our analysis reveals intriguing regularities in correlation energies across different bond types, suggesting a relationship with the atomic size. At the current stage of development, CEPB can reliably assess the accuracy of other computational methods, such as DFT-based approaches or machine learning models, particularly for very large molecules where CCSD(T) calculations entail prohibitive computational cost. Therefore, CEPB serves as a practical alternative for generating highly accurate reference data. From a machine learning perspective, our findings highlight the number and types of chemical bonds as key molecular descriptors. Furthermore, we show that two-body contributions account for 99.5% of the CCSD(T)/CBS electron correlation, recovering MP2-level accuracy for reaction energies.



P-57: SHARPENING TOOLS FOR DRUG DISCOVERY: SIZE-CONSISTENT BRILLOUIN–WIGNER SECOND ORDER PERTURBATION THEORY CALCULATIONS FOR MOLECULAR DOCKING AND QUANTUM ALGORITHMS FOR MODELING ACCURATE ELECTRONIC-VIBRATIONAL-ROTATIONAL DYNAMICS

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We present benchmark results for our implementation of size-consistent Brillouin-Wigner second-order perturbation theory (sc-BW2) by K. Fenk and M. Head-Gordon [1]. Using the IHB15 dataset, we demonstrate that sc-BW2 offers improved pose scoring compared to MP2, suggesting its potential utility in molecular docking. The computational scalability of sc-BW2 is tested through an extended benchmark with larger protein–ligand complexes, such as imidacloprid and nicotine bound to nicotinic acetylcholine receptors (nAChRs) [2], evaluated with basis sets ranging from 6-31G to def2-TZVPP, with up to 12,000 orbitals. Our in-house ***BDocker*** suite integrates sc-BW2 into virtual screening workflows, achieving a 6-10x speedup relative to the Q-Chem implementation.

Our computational vision involves addressing problems that suffer from the curse of dimensionality. To overcome this barrier in the future, we present novel fault-tolerant quantum computing algorithms for calculating full CI electronic energies using symmetry-shifted Hamiltonians and optimized tensor contraction methods [3], achieving up to 75% efficiency gains over other techniques. For accurate modeling of biochemical processes relevant to drug discovery, vibrational quantum dynamics must be included, even at room temperature. However, such simulations remain prohibitively expensive in both computational and financial terms. To address this, we propose a new quantum algorithm for simulating rovibrational quantum dynamics using general kinetic energy operators in curvilinear coordinates and non-sum-of-products potential energy surfaces. Our method utilizes discrete variable representation (DVR) [4] and Walsh-Hadamard-based quantum memory (QRAM) [5] reducing quantum resource requirements by a factor of 20-40 compared to existing techniques.

This work highlights our mission of bridging high-performance classical computational tools with emerging quantum capabilities for biochemical simulations.

[1] Carter-Fenk, K.; Shee, J.; Head-Gordon, M., J. Chem. Phys. 159 (2023), 17.
[2] Beck, M. E.; Riplinger, C.; Neese, F.; Bistoni, G., J. Comput. Chem., 42(5), (2021) 293–302.
[3] Deka, K.; Żak, E., J. Chem. Theory Comput. 21(9) (2025), 4458–4465.
[4] Pliś, S.; Żak, E., arXiv (2025), arXiv:2504.15841.
[5] Szczepanik, M.; Nagy, A.; Żak, E., (2025), in preparation.