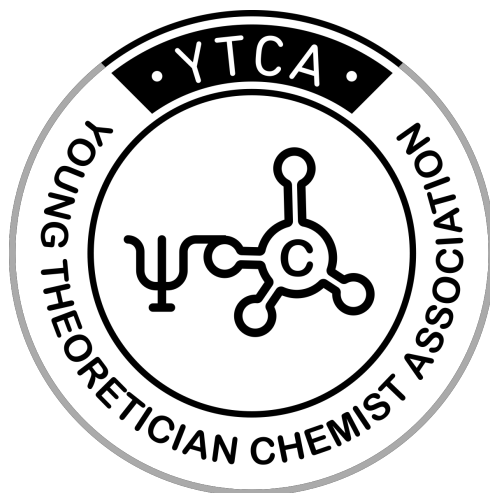UNIVERSITY OF GRAZ

ICQC 2023

Satellite Meeting

# Intermolecular Interactions and Properties of Gases, Liquids and Solids

University of Graz, Austria
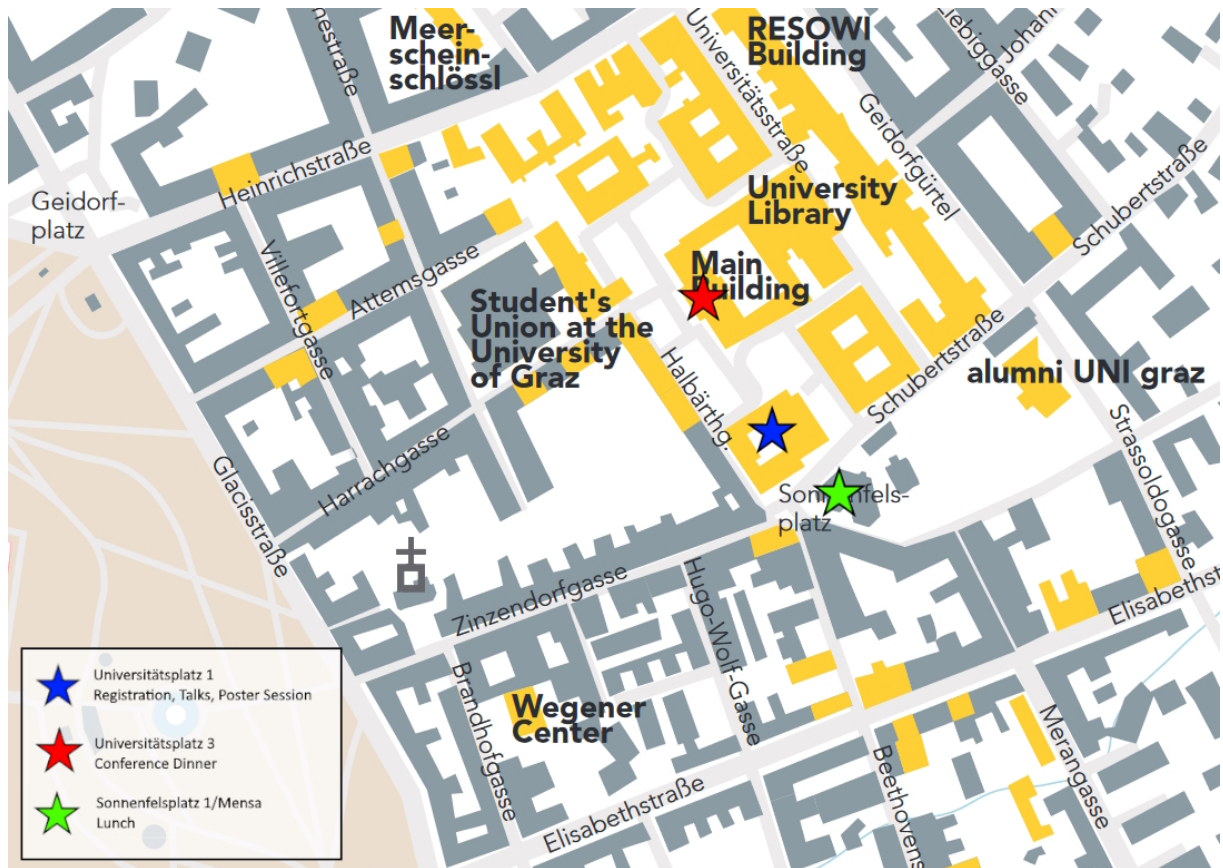
July 3-5, 2023

# Book of Abstracts

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# Conference Location



The registration, the talks, and the poster session take place at Univeristätsplatz 1, 8010 Graz. The lectures will be in room 03.01.

The lunch will be in the Mensa at Sonnenfelsplatz 1. You can choose there between the menus *Herzhaft* and *Veggie*. Lunch vouchers will be distributed at registration.

The conference dinner will be in the Aula of the university, which is located in the main building at Univeristätsplatz 3. After entering the main entrance, walk straight, take the staircase on the right to the first floor, and then turn right again.

# Program Overview

| | Monday 3rd July | | Tuesday 4th July | | Wednesday 5th July | |
|---|---|---|---|---|---|---|
| 09:00-09:20 | Registration | | Session 3 | Draxl (Chair: Beran) | Session 7 | Beran (Chair: Johnson) |
| 09:20-09:40 | | | | | | |
| 09:40-10:00 | | | | Binder | | Fink |
| 10:00-10:20 | | | | Leboucher | | Jansen |
| 10:20-10:40 | | | | Coffee break | | Coffee break |
| 10:40-11:00 | | | Session 4 | Kronik (Chair: Tkatchenko) | Session 8 | Johnson (Chair: Kelterer) |
| 11:00-11:20 | | | | | | |
| 11:20-11:40 | | | | Vöhringer-Martinez | | Hartmann |
| 11:40-12:00 | | | | Stein | | Loncaric |
| 12:00-13:00 | | | Lunch | | Lunch | |
| 13:00-13:20 | Opening Words | | | | | |
| 13:20-13:40 | Session 1 | Tkatchenko (Chair: Reuter) | | | | |
| 13:40-14:00 | | | Session 5 | Kirchner (Chair: Kronik) | Session 9 | Martin (Chair: Sax) |
| 14:00-14:20 | | Czernek | | | | Khabibrakhmanov |
| 14:20-14:40 | | Erhard | | Cervinka | | Řezáč |
| 14:40-15:00 | | Fedorov | | Huetter | | Sokalski |
| 15:00-15:20 | | Ončák | | Podewitz | | Poltavskyi |
| 15:20-15:40 | Coffee break | | Coffee break | | | |
| 15:40-16:00 | Session 2 | Reuter (Chair: Draxl) | Session 6 | Wang (Chair: Kirchner) | | Coffee break |
| 16:00-16:20 | | | | | Session 10 | Patkowski (Chair: Martin) |
| 16:20-16:40 | | Hofmann | | Rath | | |
| 16:40-17:00 | | Andrae | | Hernandez | | Hapka |
| 17:00-17:20 | | Puschnig | | Sabolovic | | Herbert |
| 17:20-17:40 | Free Time | | Free Time | | | Hoja |
| 17:40-18:30 | | | | | Closing Ceremony | |
| 18:30-19:00 | | | Conference Dinner | | | |
| 19:00-22:00 | Poster Session | | | | | |

# Scientific Program

## Monday, July 3

| 09:00 – 13:00 | | Registration |
| 13:00 – 13:20 | | Opening Words |

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Session 1 – Chair: Karsten Reuter

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| 13:20 – 14:00 | I1 | **Alexandre Tkatchenko** – University of Luxembourg, Luxembourg<br>*Fully Quantum (Bio)Molecular Simulations: Dream or Reality?* |
| 14:00 – 14:20 | C1 | **Jiří Czernek** – Institute of Macromolecular Chemistry, Czech Republic<br>*Set40: the canonical CCSD(T)/CBS interaction energies for dimers comprising up to 40 atoms* |
| 14:20 – 14:40 | C2 | **Jannis Erhard** – Friedrich Alexander Universität Erlangen, Germany<br>*$\sigma$-Functionals: a Novel Family of Correlation Functionals Yielding Chemical Accuracy at Low Computational Cost* |
| 14:40 – 15:00 | C3 | **Dmitry Fedorov** – University of Luxembourg, Luxembourg<br>*Success of the Quantum Drude Oscillator (QDO) model in describing non-covalent interactions* |
| 15:00 – 15:20 | C4 | **Milan Ončák** – Leopold-Franzens-Universität Innsbruck, Austria<br>*Small Iron-Containing Ions: Spin-Orbit Coupling, Symmetry Breaking, and Signals from Space* |
| 15:20 - 15:40 | | Coffee break |

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Session 2 – Chair: Claudia Draxl

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| 15:40 – 16:20 | I2 | **Karsten Reuter** – FHI Berlin, Germany<br>*First-Principles based Modelling of Electrocatalysis Beyond the Potential of Zero Charge* |
| 16:20 – 16:40 | C5 | **Oliver T. Hofmann** – Graz University of Technology, Austria<br>*Designing Polymorphs: The Role of the Substrate for Intermolecular Interactions* |
| 16:40 – 17:00 | C6 | **Dirk Andrae** – Freie Universität Berlin, Germany<br>*Many-to-one Mapping in Electronic Structure Calculations for Molecules and Surfaces* |
| 17:00 – 17:20 | C7 | **Peter Puschnig** – University of Graz, Austria<br>*Benchmarking density functional methods with photoemission orbital tomography* |
| 17:20 – 19:00 | | Free Time |
| 19:00 – 22:00 | | Poster Session |

## Tuesday, July 4

|  |  | Session 3 – Chair: Gregory Beran |
| --- | --- | --- |
| 09:00 – 09:40 | I3 | **Claudia Draxl** – Humboldt-Universität zu Berlin, Germany<br>*Level alignment and excitations at interfaces between molecules and 2D materials* |
| 09:40 – 10:00 | C8 | **Christian W. Binder** – Graz University of Technology, Austria<br>*Introducing Zorro – a novel code for molecular transport phenomena* |
| 10:00 – 10:20 | C9 | **Héloïse Leboucher** – University of Toulouse - Paul Sabatier, France<br>*Modeling the interaction between PAH clusters and water aggregates: structures and energetics* |
| 10:20 – 10:40 |  | Coffee break |

|  |  | Session 4 – Chair: Alexandre Tkatchenko |
| --- | --- | --- |
| 10:40 – 11:20 | I4 | **Leeor Kronik** – Weizmann Institute of Science, Israel<br>*Understanding structure-property relations in biological and bio-inspired molecular crystals from first principles* |
| 11:20 – 11:40 | C10 | **Esteban Vöhringer-Martinez** – Universidad de Concepción, Chile<br>*ffparAIM: A Python workflow for non-covalent force field parameter derivation and its applications.* |
| 11:40 – 12:00 | C11 | **Matthias Stein** – Max Planck Institute for Dynamics of Complex Technical Systems, Germany<br>*Non-covalent Interactions in Organometallic Crystals* |
| 12:00 – 13:40 |  | Lunch break |

|  |  | Session 5 – Chair: Leeor Kronik |
| --- | --- | --- |
| 13:40 – 14:20 | I5 | **Barbara Kirchner** – University of Bonn, Germany<br>*Liquid Phase Vibrational Spectra and Reducing Uncertainties in Ionic and Molecular Liquids simulation* |
| 14:20 – 14:40 | C12 | **Ctirad Cervinka** – University of Chemistry and Technology, Prague, Czechia<br>*Volatility of Ionic Liquids from First Principles: Where Experiments Can Hardly Reach* |
| 14:40 – 15:00 | C13 | **Michael Hütter** – Universität Innsbruck, Austria<br>*Master Equation Modeling of Water Dissociation in Small Ions: $Ag^+(H_2O)_n$, $n = 4\text{-}6$* |
| 15:00 – 15:20 | C14 | **Maren Podewitz** – TU Wien, Austria<br>*An Automated Approach to Quantum Chemical Microsolvation* |
| 15:20 – 15:40 |  | Coffee break |

|  |  | Session 6 – Chair: Barbara Kirchner |
| --- | --- | --- |
| 15:40 – 16:20 | I6 | **Feng Wang** – University of Arkansas, USA<br>*MP2 and DFT based ensemble property predictions rival the accuracy of experimental measurements* |
| 16:20 – 16:40 | C15 | **Gabriel Rath** – RWTH Aachen University, Germany<br>*Configuration Integral Monte Carlo Integration (CIMCI): Anharmonic Thermochemistry with Low-Cost Hamiltonians* |
| 16:40 – 17:00 | C16 | **Ramón Hernández-Lamoneda** – CIQ-IICBA/UAEM, Mexico<br>*Local structure of liquid oxygen up to supercritical conditions from ab initio pair potentials* |
| 17:00 – 17:20 | C17 | **Jasmina Savolović** – Institute for Medical Research and Occupational Health, Croatia<br>*Structure Prediction of Physiological Bis(aminoacidato)copper(II) Species in Aqueous Solution: Bis(L-glutaminato)copper(II)* |
| 17:20 – 18:30 |  | Free Time |
| 18:30 – 22:00 |  | Conference Dinner |

# Wednesday, July 5

|  |  | Session 7 – Chair: Erin R. Johnson |
| --- | --- | --- |
| 09:00 – 09:40 | I7 | **Gregory Beran** – University of California Riverside, USA<br>*Designing Organic Photomechanical Engines with Exceptional Work Capacities* |
| 09:40 – 10:00 | C18 | **Reinhold Fink** – University of Tübingen, Germany<br>*Orbital contributions explain strongly anisotropic exchange-repulsion energies and unexpected aggregate structures* |
| 10:00 – 10:20 | C19 | **Georg Jansen** – Universität Duisburg-Essen, Germany<br>*How intermolecular interactions modify the structure of $Te(BiR_2)_2$ in the solid phase* |
| 10:20 – 10:40 |  | Coffee break |

|  |  | Session 8 – Chair: Anne-Marie Kelterer |
| --- | --- | --- |
| 10:40 – 11:20 | I8 | **Erin R. Johnson** – Dalhousie University, Canada<br>*Numerical Atomic Orbital Implementation of the Exchange-Hole Dipole Moment Dispersion Model* |
| 11:20 – 11:40 | C20 | **Jessica C. Hartmann** – Universität Innsbruck, Austria<br>*Searching for the Origin of Magic Numbers amongst Sodium Chloride Clusters* |
| 11:40 – 12:00 | C21 | **Ivor Lončarić** – Ruđer Bošković Institute, Croatia<br>*Machine learning interatomic potentials for molecular crystals* |
| 12:00 – 13:40 |  | Lunch break |

| | | |
|---|---|---|
| | | Session 9 – Chair: Alexander F. Sax |
| 13:40 – 14:20 | I9 | **Jan M. L. Martin** – Weizmann Institute of Science, Israel<br>*Affordable approaches for benchmarking noncovalent interactions: localized coupled cluster theory and minimally empirical double hybrid DFT* |
| 14:20 – 14:40 | C22 | **Almaz Khabibrakhmanov** – University of Luxembourg<br>*Universal pairwise interatomic van der Waals potentials from quantum Drude oscillators* |
| 14:40 – 15:00 | C23 | **Jan Řezáč** – Institute of Organic Chemistry and Biochemistry of the CAS, Czech Republic<br>*Non-covalent interactions in semiempirical QM methods: from simple corrections to machine learning* |
| 15:00 – 15:20 | C24 | **W. Andrzej Sokalski** – Wroclaw University of Science and Technology, Poland<br>*Applications of the Theory of Intermolecular Interactions in the Rational Design of Inhibitors and Catalysts* |
| 15:20 – 15:40 | C25 | **Igor Poltavskyi** – University of Luxembourg, Luxembourg<br>*Force Field Analysis Software and Tools (FFAST)* |
| 15:40 – 16:00 | | Coffee break |

| | | |
|---|---|---|
| | | Session 10 – Chair: Jan M. L. Martin |
| 16:00 – 16:40 | I10 | **Konrad Patkowski** – Auburn University, USA<br>*Making Symmetry-Adapted Perturbation Theory More Accurate and More Robust* |
| 16:40 – 17:00 | C26 | **Michal Hapka** – University of Warsaw, Poland<br>*Symmetry-Adapted Perturbation Theory Based on Multiconfigurational Wave Function Description of Monomers* |
| 17:00 – 17:20 | C27 | **John Herbert** – The Ohio State University, USA<br>*High-Order Many-Body Expansions Via a Bottom-Up Approach* |
| 17:20 – 17:40 | C28 | **Johannes Hoja** – University of Graz, Austria<br>*Anharmonic Vibrational Frequencies of Non-Covalently Bound Systems via Vibrational Perturbation Theory* |
| 17:40 – 18:00 | | Closing Ceremony |

# List of Posters

P1 **Dirk Andrae** – Freie Universität Berlin, Germany
*Properties of Isolated Small Molecules, Molecular Ions and Molecular Clusters – Theory vs. Experiment*

P2 **Quentin Desdion** – University of Toulouse III - Paul Sabatier, France
*From micro-solvation to solvation: Study of the interaction between pesticides and water*

P3 **Natalia Goncharova** – University of Graz, Austria
*Energy Barriers of Polymorphic Transitions via First-Principles Nudged Elastic Band Calculations*

P4 **Peter E. Hartmann** – University of Graz, Austria
*Assessing Density Functional Methods for Accurate Michael Acceptor Affinities of Lewis Base Catalyzed Reactions*

P5 **Johannes Henrichsmeyer** – University of Tübingen, Germany
*Understanding exchange-repulsion with orbital contributions*

P6 **Ramón Hernández-Lamoneda** – CIQ-IICBA/UAEM, Mexico
*Computational study of the dissociation reactions of methyl acrylate on the Cu(111) surface*

P7 **Ramón Hernández-Lamoneda** – CIQ-IICBA/UAEM, Mexico
*Molecular oxygen trimer: when usually small effects become crucial*

P8 **Pulkit Joshi** – Tata Institute of Fundamental Research, India
*Generalized perturbative orbital relaxation correction based on random phase approximation*

P9 **Anne-Marie Kelterer** – Graz University of Technology, Austria
*The importance of being anharmonic: the binary system methanol-benzene*

P10 **Johannes Krondorfer** – Graz University of Technology, Austria
*Nuclear Electric Resonance for Spatially-Resolved Spin Control in Molecular Systems*

P11 **Nahoko Kuroki** – Chuo University, Japan
*Fragment-based Ab Initio Molecular Simulation and Machine Learning for Designing Interactions in $CO_2$-physisorbing Liquids*

P12 **Tilen Lindič** – Freie Universität Berlin, Germany
*Computational Study of Adsorption of CO and HF on a $NiF_2$ Surface Model*

P13 **Alexander List** – University of Graz, Austria
*Importance of Trimer Interactions for the Description of Molecular Crystals via Multimer Embedding*

P14 **Jan Ludík** – University of Chemistry and Technology, Prague, Czechia
*Development of computationally friendly procedures for solid-state organic cohesion modelling*

P15 **Ehsan Masumian** – University of Graz, Austria
*Extensive Benchmark DFT-SAPT Data Processing Reveals New Aspects*

P16 **Nichika Ozawa** – Chuo University, Japan
*Improvement of DFTB parameters toward halogen bonding interaction in drug discovery*

P17 **Khanh Ngoc Pham** – Charles University, Czech Republic
*Assessment of random phase approximation with different exchange-correlation functionals for description of binding energies of molecular solids*

P18 **Alexander F. Sax** – University of Graz, Austria
*Spin- and charge reorganization during forming and breaking of covalent bonds*

P19 **Majda Sekkal-Rahal** – University Djillali Liabes of Sidi Bel Abbes, Algeria
*Orbital Contributions to the Exchange-repulsion Energy in Donor- Acceptor Systems*

P20 **Rengel Cane Sia** – Gdańsk University of Technology, Poland
*TDDFT Investigation on a Perylene-based Logic Gate for Nitric Oxide Sensing*

P21 **Radu Alexandru Talmazan** – TU Wien, Austria
*PyConSolv: A Python Package for Conformer Generation of (Metal-Containing) Systems in Explicit Solvent*

P22 **Petr Touš** – University of Chemistry and Technology, Prague, Czechia
*A fragment-based approach for cohesion energy of crystalline ionic liquids: Doing it right*

P23 **Bartosz Tyrcha** – Nicolaus Copernicus University in Toruń, Poland
*Interaction-induced properties of weakly bound systems in the framework of symmetry-adapted perturbation theory*

P24 **Tomoko Yokaichiya** – The University of Tokyo, Japan
*Effects of Lateral Interactions on Surface Chemical Reactions Revealed by Kinetic Monte Carlo Simulations with Neural Network Potentials*

P25 **Luca Steiner** – Freie Universität Berlin, Germany
*The samarium diodide mediated diastereoselective carbon coupling mechanism*

# Abstracts: Invited Talks

# Fully Quantum (Bio)Molecular Simulations: Dream or Reality?

Alexandre Tkatchenko[a]

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The convergence between accurate quantum-mechanical (QM) models (and codes) with efficient machine learning (ML) methods seem to promise a paradigm shift in molecular simulations. Many challenging applications are now being tackled by increasingly powerful QM/ML methodologies. These include modelling covalent materials, molecules, molecular crystals, surfaces, and even whole proteins in explicit water [1]. In this talk, I attempt to provide a reality check on these recent advances and on the developments required to enable fully quantum dynamics of complex functional (bio)molecular systems. Multiple challenges are highlighted that should keep theorists in business for the foreseeable future:

(1) Ensuring the accuracy of high-level QM methods [2]

(2) Describing intricate QM long-range interactions [3, 4, 5]

(3) Treating quantum electrodynamic effects that become relevant for complex molecules [6, 7]

(4) Developing increasingly accurate, efficient, scalable, and transferable ML architectures for molecules and materials [8, 9, 10]

(5) Accounting for the quantum nature of the nuclei and the influence of external environments [11, 12]

I argue that only a conjunction of all these developments will enable the long-held dream of fully quantum (bio)molecular simulations.

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[1] O. T. Unke et al., arXiv preprint, arXiv:2205.08306 (2022).
[2] Y. S. Al-Hamdani et al., *Nat. Commun.* **12**, 3927 (2021).
[3] M. Stöhr, A. Tkatchenko, *Sci. Adv.* **5**, eaax0024 (2019).
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[10] A. Kabylda et al., *arXiv preprint*, arXiv:2209.03985 (2023).
[11] H. E. Sauceda et al., *Nat. Commun.* **12**, 442 (2021).
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# First-Principles based Modelling
# of Electrocatalysis
# Beyond the Potential of Zero Charge

Karsten Reuter

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In recent years, implicit solvation approaches have experienced a renaissance in the context of interfacial electrochemistry, not least because in conjunction with ab initio thermodynamics they allow to mimic the polarization of the electrode at potentials beyond the potential of zero charge (PZC) [1]. In this talk, I will survey this context and corresponding fully-grand canonical (FGC) calculations [2]. Specifically, I will illustrate how the FGC account of capacitive charging in the electric double layer introduces a potential-dependence of adsorption energies of closed-shell reaction intermediates [3]. Such variations are traditionally interpreted in terms of a dipole-field interaction picture. Our analysis confirms such effective dipole-field-type dependencies but rationalizes why they can neither be estimated on the basis of accessible molecular dipoles nor the mere atomic-scale geometry of the adsorption site. The observed magnitude questions mechanistic analyses of surface catalytic reactions made on the basis of the prevalent computational hydrogen electrode approach that is agnostic to these potential-induced adsorption energy variations.

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# Level alignment and excitations at interfaces between molecules and 2D materials

Claudia Draxl

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Most fascinating phenomena are observed in materials where various interactions happen on the same energy scale. Among them are organic-inorganic hybrid systems. For an *ab initio* description of their electronic excitations, all these materials are critical examples, being governed by the interplay between electron-electron interaction, electron-phonon coupling, electron-hole correlations, and potentially also spin-orbit coupling (SOC). A particular role is also played by the mutual dynamical screening of the interface constituents. With selected examples [1] I will show how hybrid and charge transfer excitations can form at such interfaces. I will also discuss the importance of forefront many-body methodology since density-functional theory (DFT) may well fail in predicting the level alignment and consequently optical and transport properties.

## References

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# Understanding structure-property relations in biological and bio-inspired molecular crystals from first principles

Leeor Kronik,[a]

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Molecular crystals are crystalline solids composed of molecules bound together by relatively weak intermolecular interactions, typically consisting of van der Waals interactions and/or hydrogen bonds. These crystals play an important role in many areas of science and engineering, ranging from biology and medicine to electronics and photovoltaics. Therefore, much effort has been dedicated to understanding their structure and properties.

Here, I will focus on our recent progress in explaining and even predicting important classes of collective effects, i.e., phenomena that the individual units comprising the crystal do not exhibit, but arise through their interaction. Specifically, I will demonstrate these concepts by addressing: (1) Structure and (mostly) optical function relations in biogenic molecular crystals; (2) Surprising mechanical properties of bio-inspired molecular crystals; (3) Unexpected magnetic and spintronic behavior in metal-organic crystals. Throughout, I will highlight the insights gained from a successful interaction between theory and experiment.

# Liquid Phase Vibrational Spectra and Reducing Uncertainties in Ionic and Molecular Liquids simulation

Barbara Kirchner

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We will present our recent developments for the calculation of infrared,[1] Raman,[1] and vibrational circular dichroism [2, 3] spectra of flexible molecules in non-idle environments. [4] The calculation of such spectra requires: 1) a realistic description of the environment and 2) a sufficient sampling of the solvation shells and molecular conformations. We will show how these critical issues can be addressed to obtain robust predictions of liquid phase spectra. We further present applications of our methods to study chiral phenomena, e.g. asymmetrization and chirality transfer in (ionic) liquids, which can be used to develop new chiral selectors and separation processes.[5, 6] This will be accompanied by the investigation of uncertainties in modellling liquid properties.[7]

# References

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# MP2 and DFT based ensemble property predictions rival the accuracy of experimental measurements

Dong Zheng,[a] Ying Yuan[a] and Feng Wang[a]

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Computing free energies and other ensemble properties with electronic structure methods are challenging due to the need to sample rough potential energy surface (PES) with many degrees of freedom. With the adaptive force matching (AFM) approach,[1] electronic structure PES at MP2, LMP2, and DFT levels of theory are fitted to molecular mechanics energy expressions. [2,3] No combining rules are used with AFM models for the faithful representation of short-range interactions between pairs of atoms. Without the restrictions inherent in combining rules, AFM models provide sufficient accuracy to predict reliable ensemble properties, such as hydration free energies, enthalpies of hydration, and diffusion constants for various salts and small drug-like molecules with up to 30 atoms.[4,5] Some discrepancies in the theoretical predictions were tracked down to unreliable experimental numbers or complications when comparing theoretical and experimental values. For hydrated polypeptides, the DFT based conformational distribution is in excellent agreement with experimental NMR scalar coupling data.[6] It is shown that B3LYP provides good accuracy for hydration free energies and the use of at least a triple-zeta quality basis set, such as def2-TZVP, is important to reach chemical accuracy.

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6.  Y. Yuan, Z. Ma, F. Wang, *J. Phys. Chem. B.,* **125**, 1568 (2021).

# Designing Organic Photomechanical Engines with Exceptional Work Capacities

Gregory Beran,[a]

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Organic photomechanical crystals transform light into mechanical work, with work densities that are 2-3 orders of magnitude higher than those of piezoelectrics or elastomers. While many photomechanically active species have been identified, little is known experimentally about the relationship among molecular species, photochemical reaction, crystal structure, and mechanical work, and this lack of knowledge has hindered the development of more practical materials. To establish design rules that can guide the experimental development of photomechanical crystals, we have developed a new theoretical approach that predicts the crystal structures of the reactant species, the solid-state photochemical transformation, and the maximum ideal work that could be performed by the system. We harness reliable crystal structure prediction methods, address the impacts of density functional theory delocalization error, and establish a thermodynamic cycle for idealized solid-state photomechanical engines.

Using these approaches to study diarylethene and anthracene materials,[1, 2] we (1) demonstrate how crystal packing is far more important to photomechanical performance than has been recognized previously, with the work density for different crystal polymorphs of the same species ranging over an order of magnitude, (2) identify crystal packing features that produce high work capacities, and (3) identify an inherent asymmetry that biases photomechanical engines to produce greater work on the forward stroke than the reverse stroke. The resulting design principles provide guidance for improving experimental photomechanical engines.

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# Numerical Atomic Orbital Implementation of the Exchange-Hole Dipole Moment Dispersion Model

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Inclusion of London dispersion in density-functional calculations is now standard practice in computational chemistry and materials science. While there are a number of density-functional dispersion corrections, this talk will focus on the exchange-hole dipole moment (XDM) model, which is an asymptotic method based on second-order perturbation theory. The XDM dispersion coefficients are non-empirical and depend directly on the electron density and related properties, allowing for variation with changing atomic environment. XDM offers simultaneous high accuracy for a diverse range of chemical systems, such as intermolecular complexes, molecular crystals, and layered materials. This talk will focus on a recent implementation of XDM in the Fritz Haber Institute *ab initio* materials simulations (FHI-aims) software package [1]. The FHI-aims code uses atom-centered numerical atomic orbitals as basis functions, allowing efficient calculations on periodic systems with large unit cells, even using hybrid density functionals. Performance for molecular crystals will be highlighted, including the X23 benchmark of lattice energies, a set of 13 ice polymorphs, and the compounds forming the first six blind tests of molecular crystal structure prediction [1, 2].

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# Affordable approaches for benchmarking noncovalent interactions: localized coupled cluster theory and minimally empirical double hybrid DFT

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Despite recent advances in density functional theory, there remains a need for accurate calibration in general, and for noncovalent interactions in particular. While explicitly correlated coupled cluster theory is clearly able to fulfill this goal, its steep CPU time scaling with system size makes the canonical variant cost-prohibitive for all but the smallest systems. Localized coupled cluster approaches[1,2,3] potentially offer succor, as they asymptotically scale linearly with system size. We show[4] for the Hobza S66x8 noncovalent benchmark (against revised benchmark values[4]) and for alkane conformers[5] that with judicious domain cutoff and extrapolation settings, composite localized coupled cluster schemes are quite capable of supplying such accuracy. Some caveats concerning the treatment of basis set superposition error are in order though.

Minimally empirical double hybrid approaches[6,7] turn out to perform quite well for noncovalent interactions. When using a RI approximation, the second-order perturbation theory term only constitutes a tiny percentage of total CPU time for smaller systems, but owing to its steeper scaling will eventually dominate the total. Fortunately, said term can be linearized by means of orbital localization[8] while even an *spd* basis is adequate for this term if F12 geminals are added[9].

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# Making Symmetry-Adapted Perturbation Theory More Accurate and More Robust

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Symmetry-adapted perturbation theory (SAPT) is a well established approach to computing intermolecular interaction energies and analyzing them in terms of physical contributions such as electrostatics, induction, dispersion, and exchange. In the SAPT decomposition, intermolecular electron correlation gives rise to the second- and higher-order dispersion and exchange-dispersion terms, while intramolecular correlation can be taken into account by a perturbation series, density functional theory, or coupled-cluster treatments. In recent years, many extensions to SAPT have been proposed to achieve higher accuracy and applicability to a wider range of problems. Several of these extensions are pursued in our research group: (1) the explicitly correlated (F12) treatment of intermolecular electron correlation to improve basis set convergence [1], (2) the removal of the conventional single exchange approximation from higher-order SAPT terms, eliminating short-range artifacts of some SAPT variants [2], (3) an estimate of splittings between different spin states of an open-shell interacting complex within the "spin-flip SAPT" framework [3], and (4) attempts to provide a consistent and robust SAPT decomposition of intramolecular noncovalent interactions [4].

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# Abstracts: Contributed Talks

# Set40: the canonical CCSD(T)/CBS interaction energies for dimers comprising up to 40 atoms

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There is an everlasting interest in accurate predictions of the intermolecular interaction energy, $\Delta E$. Benchmark $\Delta E$ vales for mid-sized complexes (with several dozens of atoms) are scarce. This is why we employed data from our recent study of dissociation energies of dimers comprising up to 32 atoms [1] and considered even larger systems, namely, 8 configurations of 9H-xanthene:phenol (38 atoms in total) [2] and 11 configurations of 9H-xanthene:toluene (40 atoms) [2], and for a total of 40 complexes we compiled the energies for an estimation of the canonical CCSD(T)/CBS $\Delta E$ using a focal-point approach. All 40 complexes of the resulting data set (called Set40) were investigated in a high-level geometry, and their intermolecular bonding was characterized by the SAPT-DFT/CBS analysis. The reference $\Delta E$ values from the Set40 span a large interval from ca. –89 to –6 kJ/mol. Numerous methods less demanding computationally were applied to this set. Interestingly, the ωB97X-3c/vDZP approach most recently proposed by Grimme at al. [3], which is computationally very cheap, was found to perform well (see the graphics below). This is important for $\Delta E$ predictions in extended systems like models of polymer chains or biomaterials.
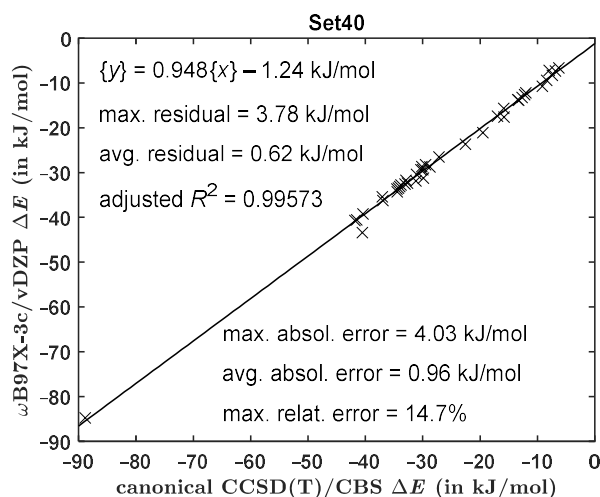


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# C2

# $\sigma$-Functionals: a Novel Family of Correlation Functionals Yielding Chemical Accuracy at Low Computational Cost

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An highly active area of research in density-functional theory (DFT) is the development of functionals for the Kohn-Sham correlation energy that are based on the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem[1]. Within the ACFD theorem, a hierarchy of correlation functionals with increasing accuracy can be constructed [2]. The crucial quantity to approximate in ACFD functionals is the exchange-correlation kernel, the functional derivative of the exchange-correlation potential. The simplest case is the random phase approximation (RPA), which neglects the exchange-correlation kernel and takes into account exclusively the known Hartree kernel. If additionally the exchange kernel is considered the EXXRPA approach results. If the correlation kernel is modeled by the Hartree or the sum of Hartree and exchange kernel then functionals named $\sigma$- and $\tau$-functionals, respectively, emerge. The first $\tau$-functional was based on a power series of the correlation kernel [3], showed high accuracy but was applicable only to small systems due to its computational cost. Recently developed $\sigma$-functionals [4] require a computational effort lower than that of standard hybrid functionals but yield chemical accuracy of about 1 kcal in reaction energies in main group chemistry and take into account dispersion interaction in a seamless way. In scaled $\sigma$-functionals [5] information from the homogeneous electron gas on scaling relations between the Hartree and the exchange kernel is incorporated to further improve the functionals without significantly increasing the computational effort. Scaled $\sigma$ functionals, e.g., yield ionization energies with a higher accuracy than CCSD(T) methods. $\sigma$-Functionals have been incorporated in various programm packages (Molpro, TURBOMOLE, ADF, VASP, FermiONs++ [6], PySCF). Here an introduction to ACFD functionals and their performance is given.

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C3

# Success of the Quantum Drude Oscillator (QDO) model in describing non-covalent interactions

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Electronic-structure methods can serve as a robust tool for modeling molecules and materials, and they are widely used to describe both covalent and non-covalent interactions. However, in order to efficiently capture non-covalent interactions in large molecules and extended materials, it is advantageous to switch to coarse-grained approaches. A particularly efficient and accurate approach for electronic correlations is the Quantum Drude Oscillator (QDO) model [1] with its extension to many-body effects [2], that has been successfully applied to describe the polarization and van der Waals (vdW) interactions in a multitude of systems. We give a short overview on fundamental as well as practical aspects of the QDO model for the electronic response in atoms and molecules. Among them, a number of our own contributions to the recent development of the QDO model will be discussed: introducing the coarse-grained exchange interaction into this model within [3] or beyond [4] the dipole-dipole approximation; using QDOs for coarse-grained description of non-covalent interactions under internal/external static electric fields in/between molecules [5,6]. We also discuss how the properties of the QDO model allow to unveil a remarkable quantum-mechanical scaling law between the electronic polarizability and either vdW radii of interacting atoms [3,7] or geometric volumes of isolated atoms [8].

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# Small Iron-Containing Ions:
# Spin-Orbit Coupling, Symmetry Breaking, and
# Signals from Space

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Transition metals are of pivotal importance in catalysis due to their complicated electronic structure with multiple close-lying electronic states (whose relative stability can be influenced through chemical environment), several stable oxidation states, and pronounced spin-orbit coupling effects. The very same properties make their modeling quite challenging, requiring multi-reference methods for photochemical calculations and explicit treatment of electronic states of various spin multiplicities already for reactivity at room temperature due to multiple-state reactivity.

In the present contribution, I will review our recent work on photochemistry of small iron-containing ions, namely $FeH^+Ar_n$, $n = 0$–2,[1] $Fe^+(H_2)_m$, $m = 1$–2, and $Fe^+(H_2O)$. These systems are of astrophysical importance, but serve also as models for understanding electronic structure of compounds with transition metals under well-defined experimental conditions. The ions were investigated employing Fourier-Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry combined with laser irradiation in a broad range of ~0.5–5.5 eV. The electronic spectra were modeled employing reflection principle approximation and multi-reference configuration interaction (MRCI) with explicit inclusion of spin-orbit effects. Among other findings, we show how argon tagging considerably influences the electronic structure through symmetry breaking.

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# Designing Polymorphs: The Role of the Substrate for Intermolecular Interactions

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Interfaces between conductive inorganic substrates and organic molecules play an important role for organic electronics, including mobile phone displays or photovoltaic cells. A significant advantage over conventional materials is that the properties of the interfaces can be meticulously tuned to the application. Hereby, not only the chemical nature of the organic molecule, but also the structure (i.e., the polymorph) it assumes on the surface are decisive.

We have recently developed a specialized structure search code,[1] that allows us to predict which polymorph a given organic/inorganic interface forms. Relying on only ~200 well-selected DFT calculations, it employs machine learning in the form of Bayes Linear Regression to determine the possible molecule-substrate and intermolecular interactions, and, in turn, provides a list of relative polymorph stabilities.

Applying this strategy to a set of homologue acenequinones allows us to deduce general structure-to-property relationships and thus design principles for molecules, which can be exploited to favor or disfavor selected polymorphs.[2] However, going beyond simple molecular design, the method also allows us to determine how the substrate on which the organic growth impacts the intermolecular interactions. We show that by choosing the right kind of substrate, it is possible to systematically benefit systems with high charge-carrier mobilities. [3] To change the intermolecular interaction direct contact is not even necessary – even for growth on 2D semiconductors like hexagonal boron-nitride, the underlying support can be systematically exploited to select which structure forms. [4]

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# Many-to-one Mapping in Electronic Structure Calculations for Molecules and Surfaces

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"There is nothing more practical than a good theory [...]" [1] — Problems of many-to-one mapping in electronic structure calculations are related to degeneracies, which are themselves a consequence of the symmetry of the system under study: A common energy (eigen)value is assigned to several electronic states of the system. Reduction of symmetry (e. g. via distortion) leads then to an at least partial removal of degeneracies. I will discuss, example by example, a few cases where degeneracy due to symmetry plays an important role in molecular electronic structure, in bond formation / dissociation processes and in molecule–surface interaction processes. Convenient handling of degeneracies still poses challenges to computational methods. But, in view of Ahlrichs' quote, the theory of symmetry turns out to be an exceptionally practical theory, although it does not yield complete solutions of electronic structure problems.

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# C7

# Benchmarking density functional methods with photoemission orbital tomography

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In the past decade, photoemission orbital tomography (POT) has evolved into a powerful tool to investigate the electronic structure of organic molecules adsorbed on surfaces. By measuring the angular distribution of photoelectrons as a function of binding energy and making use of the momentum-space signature of molecular orbitals, POT leads to an orbital-resolved picture of the electronic density of states at the organic/metal interface [1]. In this combined experimental and theoretical work, we apply POT to the prototypical organic $\pi$-conjugated molecule bisanthene ($C_{28}H_{14}$) which forms a highly oriented monolayer on a Cu(110) surface [2]. Experimentally, we identify an unprecedented number of 13 $\pi$ and 12 $\sigma$ orbitals of bisanthene and measure their respective binding energies and spectral lineshapes at the bisanthene/Cu(110) interface. Theoretically, we perform density functional calculations for this interface employing four widely used exchange-correlation functionals from the families of the generalized gradient approximations as well as global and range-separated hybrid functionals. By analyzing the electronic structure in terms of orbital-projected density of states, we arrive at a detailed orbital-by-orbital assessment of theory vs. experiment. This allows us to benchmark the performance of the investigated functionals with regards to their capability of accounting for the orbital energy alignment at organic/metal interfaces [3].

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# Introducing Zorro – a novel code for molecular transport phenomena

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Molecular diffusion and storage within porous structures is a compelling subject of study due to its diverse array of associated applications. These include seawater desalination, industrial scale gas separation, chiral separation of drug molecules via two-dimensional materials like porous graphene or flat metal-organic frameworks, and gas storage in structures such as zeolites. However, providing an ab initio description of these processes remains a daunting task given the highly disordered and complex nature of molecular propagation, often characterized by seemingly random trajectories. Currently, the established standard for theoretical estimates of permeabilities and diffusion constants relies on molecular dynamics simulations utilizing cost-effective force fields. Nonetheless, these force fields often lead to significant prediction errors in energy, thereby distorting the true values by orders of magnitude.

A method will be introduced that tackles the aforementioned challenges by employing the knowledge of molecular partition sums, thereby potentially replacing molecular dynamics simulations. Moreover, a novel programming package, dubbed Zorro (**Z**ustandssummen **o**f **R**igid **R**otor **O**bjects), will be discussed. This computational tool facilitates a cost-effective determination of molecular partition sums. Consequently, it enables the application of high-level methods such as density functional theory (DFT) while preserving the methodological accuracy inherent to molecular dynamics simulations. By doing so, Zorro lays the foundation for a broader application of partition sum-based methods to other types of molecular diffusion-related problems.

1.  Christian W. Binder, Johannes Krondorfer and Andreas W. Hauser, *Molecular Systems Design & Engineering* **7**, 1622 - 1638 (2022).

# Modeling the interaction between PAH clusters and water aggregates: structures and energetics

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Polycyclic aromatic hydrocarbons (PAHs) are a family of molecules that have multiple research interests, especially in atmospheric science and in astrophysics/astrochemistry. Forty years ago, PAHs were proposed as the carriers of the aromatic infrared bands (AIBs), observed in many regions of the interstellar medium (ISM) [1, 2]. Moreover, it is believed that in the colder and denser regions of the ISM, PAHs could freeze on the icy mantle of interstellar dust grains and interact with other molecules like water [3]. In this context, it is relevant to characterize theoretically and experimentally the interactions involved in PAH-water clusters.
We present here a theoretical study to characterize the interactions of the dimer of pyrene (Py), $C_{16}H_{10}$, with water clusters. Previous works focused on pyrene clusters on one hand [4], and on the interactions of a single PAH with water clusters on the other hand [5, 6]. In this work, we report the investigation of $(Py)_2(H_2O)_n$ ($n = 1, 10$) systems in the gas phase [7].

We used the following strategy to search for the most stable structures. First, Parallel-Tempering Monte-Carlo (PTMC) simulations were performed to explore the potential energy surfaces of these clusters, using the density-functional based tight-binding (DFTB) electronic structure method. This potential was improved to describe correctly long-range electrostatic and dispersion interactions. All-atom optimisations were then performed, with the same DFTB potential, and the lowest-energy structures were refined with DFT (density functional theory). For the lowest stoichiometries ($n = 1, 5$), a competition was found between the structures where the water cluster interacts on the side of the pyrene molecules ($\sigma$ interactions) and the ones with the water cluster above the pyrene molecules ($\pi$ interactions). Other kinds of competition arise for the highest stoichiometries ($n = 6, 10$), and we notice a beginning of a solvation cage with the largest water clusters. The energetics of several *a priori* competitive dissociation channels were explored and "magic numbers" (i.e. particularly stable sizes) were determined. We manage to interpret the energetic trends based on the different structural arrangements of the clusters.

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# ffparAIM: A Python workflow for non-covalent force field parameter derivation and its applications.

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We introduce a methodology based on the QM/MM methodology and the Minimal Basis Iterative Stockholder (MBIS) partitioning of the polarized electron density to derive atomic charges and Lennard-Jones (LJ) parameters of molecules in condensed phases. Our Python-based protocol combines molecular dynamics simulation carried out with OpenMM and the QM/MM approach to obtain force field paramaters from several configurations of the trajectory. Electron densities can be obtained for every level of theory and basis set available in ORCA 5.0.1 software. Combining IOData[1] and other libraries from the Horton3 package, we derive atomic charges and effective atom volumes partitioning the polarized electron density of each configuration with the MBIS method. Values are averaged from all extracted configurations and replaced in the topology before initialization of a new cycle of MD simulations and QM/MM calculations until convergence. Bond-based symmetrization and atom type correction is considered for the final topology output.

The new derived non-covalent force field parameters were validated with host-guest systems, which are widely in computational binding affinity prediction. These predictions are mainly limited by the accuracy of the force fields. This workflow was applied in two octa acid and cucurbit[7]uril hosts that bind chemically diverse guests. Alchemical free energy calculations with the YANK software package reveal that MBIS atomic charges improve the prediction for all host-guest systems whereas LJ parameters become relevant for guests with adamantyl core binding to CB7 host.[2]

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# Non-covalent Interactions in Organometallic Crystals

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Organometallic complexes are the basis for homogeneous catalysis, have applications in materials science and are active pharmaceutical ingredients. The interaction between transition metal complexes in the solid state is determining their thermodynamics and bio-availability.

Whereas the stabilizing contributions of hydrogen bonding and van-der-Waals interactions are reasonably well understood [1, 2], non-covalent organometallic crystals are less explored.

The variation of ligand field, central metal atoms and their oxidation and spin states are determinants of the magnitude of their inter-molecular interactions. A comparison of a set of 43 manually curated experimental heats of sublimation (the new XTMC43 set) and results from periodic DFT calculations shows that an agreement to within a few percent can be achieved using GGA or mGGA functionals with atom-centred Gaussian-type basis functions.

The need for careful assessments of consistency, calibration and reproducibility of experimental and computational data is discussed. Results regarding the new XTMC43 benchmark set are suggested to serve as a starting point for further method development, systematic screening and crystal engineering.

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# Volatility of Ionic Liquids from First Principles: Where Experiments Can Hardly Reach

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Ionic liquids have been considered non-volatile for long. Even after demonstrations of distillation of ionic liquids, experimental challenges still impede reliable determination of vapor pressures for these materials [1], which typically suffer from a severe inter-laboratory disagreement [2]. Despite ranging to the sub-pascal region at ambient conditions, such low vapor pressures are sufficient for global atmospheric spread in case of large-scale applications or leaks of ionic liquids to the environment.

First-principles calculations can, on the other hand, provide relatively accurate models of sublimation of molecular crystals [3]. Exploiting the crystal structure of ionic liquids, one can reach the sublimation enthalpy and the pressure coordinate of the crystal-liquid-vapor triple point *in silico*. Fragment-based ab initio models can be then employed to refine the cohesive energy of the crystal, although this process is not risk-free for such strongly-bound materials as crystals of ionic liquids. Summation of the computed sublimation enthalpy with the enthalpy of fusion, being accurately measurable or accessible from MD simulations [4], then yields the vaporization enthalpy of the liquid, itself being hardly measureable at ambient conditions [2].

This work develops quasi-harmonic DFT models of cohesion and phonons of crystalline aprotic ionic liquids [5] and a hybrid QM:MM model of thermodynamic properties of vapors of ionic liquids [2]. All those are then applied to model structural and thermodynamic properties and sublimation of three archetypal 1-ethyl-3-methylimidazolium ionic liquids. We demonstrate that the DFT-D/PAW calculations capture the sublimation enthalpy with an uncertainty about 10%, corresponding to roughly 15 kJ/mol. Since the literature experimental data on sublimation enthalpies for these materials are scattered over 20 kJ/mol, the underlying DFT-D/PAW calculations of the sublimation enthalpy fit within such a range.

However, a critical data assessment and a simultaneous correlation enables to develop reference data with the state-of-the-art sub-chemical accuracy when experimental data are abundant enough in the literature [2]. To further improve the quality of the predicted sublimation enthalpy at least to the chemical accuracy level, and to approach the real experimental accuracy, fragment-based methods are applied and their accuracy is discussed.

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# Master Equation Modeling of Water Dissociation in Small Ions: $Ag^+(H_2O)_n$, $n$ = 4-6

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The intricate electronic structure of noncovalent metal ion complexes, leading to numerous chemical and physical properties, has been the focus of intense investigation due to their role in various catalytic mechanisms in both biological and industrial domains. In this study, we investigated a gas phase model for solvated silver cation $Ag^+(H_2O)_n$, with $n$ = 4–6, employing Master Equation Modeling (MEM) for the calculation of Blackbody Infrared Radiative Dissociation (BIRD) rates, and compared these to previously conducted experimental measurements [1].

The unique physical properties of these clusters lead to the existence of several low-energy isomers, introducing considerable complexity in the accurate calculation of energetics via MEM. To pinpoint and precisely incorporate these isomers within the MEM framework, we employed a custom-designed Genetic Algorithm (GA) for a global optimization search approach, used in conjunction with a recently developed multiple-well method for MEM [2]. Our results underscore the importance of including multiple isomers for accurate energetics predictions.

Further, we explored two models to characterize transitional modes within the RRKM framework for dissociation, as used in MEM, namely the rigid activated complex (RAC) RRKM model and the phase space limit (PSL), concluding that the PSL model corresponds more closely to the experimental rates, supporting the argument for weakly bound ligands. Therefore, we conducted additional molecular dynamics simulations for various internal energies in the NVE ensemble, aiding further insight into ligand displacement from equilibrium positions and the possibilities for isomerization.

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# An Automated Approach to Quantum Chemical Microsolvation

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Chemical reactions often take place in the liquid phase, which are best described using condensed phase calculations. Fully quantum chemical treatment of such systems is often impractical, leading to the use of implicit solvent methods that model bulk solvent properties. However, these methods fail when explicit solute-solvent interactions significantly affect the molecule's conformation and reactivity.

To address this limitation, microsolvation methods emerged, taking only the most relevant solvent molecules into account for quantum chemical calculations. However, defining the number and exact location of solvent molecules has remained ambiguous. We have developed a physics-based approach to quantum chemical microsolvation, where we deduce the number, location, and orientation of solvent molecules in an automated manner. This is achieved by utilizing the free energy of solvation, derived from Molecular Dynamics (MD) simulations and Grid Inhomogeneous Solvation Theory.[1] Our procedure rigorously defines the number, positions, and orientations of individual solvent molecules for subsequent quantum chemical investigations (see Figure 1).[1,2] We demonstrate the applicability of our methodology with various biologically relevant or biomimetic molecules. Our approach is robust and our results comparable to *ab initio* and experimental data.
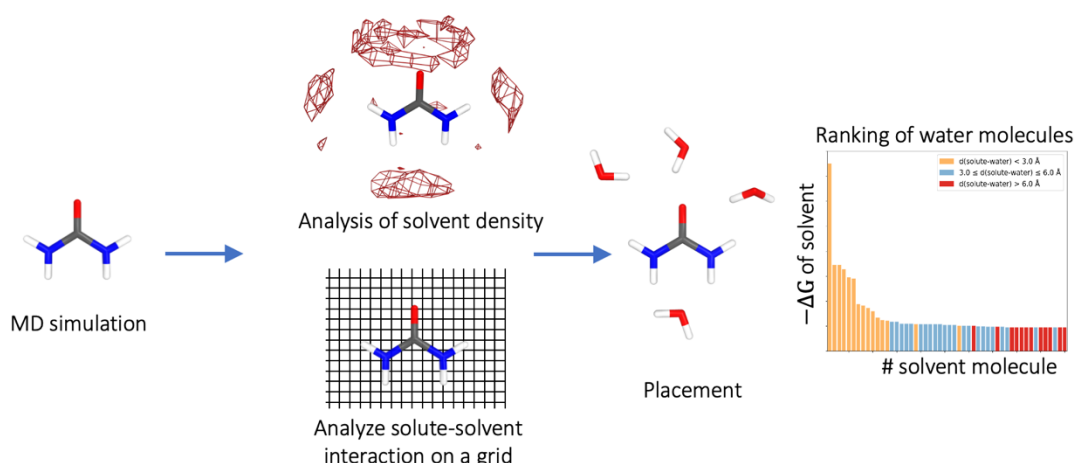


**Figure.** Workflow to yield microsolvated structures for subsequent quantum chemical calculations.

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# Configuration Integral Monte Carlo Integration (CIMCI): Anharmonic Thermochemistry with Low-Cost Hamiltonians

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There is a major ongoing drive to accurately predict thermochemical data to better model atmospheric, industrial, and combustion processes. Contributions to these efforts tend to focus either on high-quality Hamiltonians for electronic properties or on modeling the motion of nuclei. For the latter, most state-of-the-art approaches rely on the same, core process of approximations to tackle the common set of challenges posed when dealing with the high-dimensional potential energy surface (PES) of a sufficiently accurate, high-quality *ab initio* Hamiltonian. These maintain high accuracy in the electronic model at the cost of a lower accuracy model for nuclear motions, which can introduce major errors for data of certain systems prone to fluctional motions.

However, alternative approaches are possible with a different trade-off. Rather than make bespoke, localized approximations on-the-fly, one can use a PES of an approximate Hamiltonian that is fast enough to be sampled broadly, *e.g.*, force fields, semi-empirical methods, or machine learning potentials, and numerically integrate them over thermally accessible regions. This sacrifices some accuracy in the electronic model to gain significantly more accuracy in the modeling of nuclear motions, which can be worth it for the aforementioned fluctional systems.

Configuration Integral Monte Carlo Integration (CIMCI) [1] is a recently published method taking this approach. It uses an enhanced version of MISER [2] Monte Carlo integration to perform the necessary high-dimensional integration in a fully classical space, then applies the Pitzer-Gwinn correction [3] to correct for quantum effects. Its ultimate goal is to provide a black-box method by which any compound with any kinds of anharmonicities can be handled to a reasonable degree. The few fluctional systems for which proper reference data are available show CIMCI performing very well even with a very coarse Hamiltonian like UFF [4]. *E.g.*, compared to M06-2X/cc-pVTZ [5], UFF with CIMCI gives anharmonic entropy correction factors for $H_2O_2$ that are better than VPT2 and on par with explicit 1D hindered rotor handling. Absolute standard molar entropies with UFF with CIMCI are also closer to reference data than CCSD(T)/aug-cc-pVQZ coupled cluster with RRHO. MISER and its enhancements are crucial to the practicality of CIMCI: MISER alone reduces computational costs by around 2-3 orders of magnitude, and the novel enhancements to MISER reduce these computational times by a further 2-3 orders of magnitude.

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# Local structure of liquid oxygen up to supercritical conditions from *ab initio* pair potentials

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The local structure and orientational correlations of liquid oxygen up to supercritical conditions have been determined using highly accurate *ab initio* pair potentials[1,2] and a spin-average approximation. The predicted radial distribution functions are in excellent agreement with all the available experimental data[3,4] covering a wide range of temperatures and pressures, something which could not be accomplished in any previous studies of this type[5]. In particular the elusive shoulder characteristic of several diatomic fluids is accurately reproduced and more importantly its true origin elucidated by performing an exhaustive analysis of the orientational correlations indicating the relevance of specific configurations which had not been taken into account before.

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# Structure Prediction of Physiological Bis(aminoacidato)copper(II) Species in Aqueous Solution: Bis(L-glutaminato)copper(II)

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The electrically neutral bis(aminoacidato)copper(II) compounds are the physiological species present in blood plasma. They are supposed to take part in the transport and storage of the copper(II) ions. Although several X-ray crystal and molecular structures of these low-molecular-weight compounds were determined, generally their complete structural properties in solutions cannot yet be derived by experimental methods. The structural properties predicted by molecular modelling methods can thus complement the experimental findings.

This paper reports a density functional theory study of the structural properties of bis(glutaminato)copper(II) in the gas phase and in implicitly modeled aqueous solution using a polarizable continuum model (PCM). The energy landscapes of the isolated and aqueous compound are compared to rationalize the impact of aqueous environment on the stability of coordination modes and overall geometries relative to the gas phase. The much larger number of aqueous conformers compared to the gaseous ones suggests that aqueous surroundings stabilize the conformers that are unstable in the gas phase. The conformers with both the *trans*- and *cis*-configuration have a similar stability in aqueous solution, while the *trans* conformers are energetically more stable than the *cis* ones as isolated compounds.

The reliability of predicted lower-energy aqueous conformers is tested by comparing the calculated magnetic parameters with experimental electron paramagnetic resonance parameters measured in an aqueous solution [1]. Good reproduction is obtained for the *trans* and *cis* conformers with two oxygen atoms (either from L-glutamine or explicit water molecules) at the apical positions, which supports the experimental evidence for the presence of both isomers in aqueous solution at ambient temperature [1].

The experimental X-ray crystal structure of the title compound [2] was used as the starting structure for the geometry optimization in simulated aqueous surroundings to examine whether noncovalent interactions simulated by PCM can cause the same effect on the bis(L-glutaminato)copper(II) geometry as the crystal lattice effects do.

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# Orbital contributions explain strongly anisotropic exchange-repulsion energies and unexpected aggregate structures

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The structures of prototypical non-covalently bonded systems with $\pi$-stacking or halogen-bonding interactions are shown to be decisively influenced by anisotropies of the exchange-repulsion energy, $E_{\text{exr}}$. We demonstrate [1] that the underlying reason is the quantum-mechanical origin of $E_{\text{exr}}$ and the wave nature of the occupied orbitals contributing to it. This is rationalised by rewriting an established expression for the exchange-repulsion energy [2] as

$$E_{\text{exr}} = \sum_{ab} E_{\text{exr}}(a, b), \tag{1}$$

where $a$ and $b$ represent the occupied orbitals of the two interacting systems. The orbital contributions $E_{\text{exr}}(a, b)$ are repulsive when the orbital overlap is significantly different from zero, but slightly attractive for non-overlapping orbitals. The latter can occur even for nearly spaced orbitals if the lobes of one orbital point to nodes of the other one or, more generally, if the respective wavefunctions are non-coherent. We demonstrate that such structures show reduced exchange-repulsion and frequently correspond to minima of the respective intermolecular potential energy surfaces.

These considerations explain the well-known parallel-shifted arrangements of $\pi$-stacked aromatic systems and its halogenated derivatives where common explanations based on electrostatic interactions fail. The latter is in particular the case [3] for the frequently used Hunter-Sanders model [4]. Orbital contributions to the exchange-repulsion energy do also explain the strong preference of halogen bonds for linear arrangement and crystal structures of donor-acceptor systems such as benzene-benzoquinone or naphtalene-TCNE.

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# How intermolecular interactions modify the structure of Te(BiR$_2$)$_2$ in the solid phase

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With large static dipole polarizabilities ($>$ 40 a.u., [1]) heavy group 15 atoms atoms can be expected to act as good London dispersion energy donors, while on the other hand their relatively large van der Waals radii ($>$ 2.0 Å, [2]) signalise early onset of steric repulsion. They thus appear to be good candidates for experimental and theoretical studies of the interplay between attractive and repulsive contributions to non-covalent interactions between atoms. In particular, it was found [3, 4] that metal-organic compounds containing two group 15 heavy metal atoms linked by a bridging group 14 atom may display distances between the metal atoms which come close to or even fall below the sum of their van der Waals radii, and that the corresponding bond angles may become significantly smaller than 90$^\circ$.

Here we focus on Te(BiR$_2$)$_2$ (R = H, Me, Et) [5, 6], characterizing interactions between the metal atoms through various quantum chemical methods including dispersion-corrected density functional, (local) coupled cluster, and symmetry-adapted perturbation theory. Significant deviations of the computed gas phase Te-Bi bond length by more than 0.14 Å and of the Bi-Te-Bi bond angle by more than 3$^\circ$ from the corresponding parameters observed in X-ray crystallography are shown to be due to the influence of neighbouring molecules in the crystal, highlighting the role of charge transfer and dispersion interactions.

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# C20

# Searching for the Origin of Magic Numbers amongst Sodium Chloride Clusters

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As one of the main components of sea salt aerosols, sodium chloride is involved in numerous atmospheric processes such as cloud formation and photochemical as well as chemical reactions, significantly affecting the climate on Earth [1]. Gas phase clusters are ideal models to study fundamental physical and chemical properties of sodium chloride. According to previous studies [2], these properties are significantly affected by the cluster size. Of particular interest are magic cluster sizes, which exhibit high intensities in mass spectra.

In order to understand this size dependency, we performed a combined experimental-theoretical study, focusing on the relative stability as well as their dissociation behavior. In contrast to earlier studies [3], our calculations show that the binding energy of a single NaCl unit or the respective ion ($Na^+$ or $Cl^-$) to the smallest anionic $(NaCl)_x Cl^-$ and cationic $(NaCl)_x Na^+$ magic cluster with $x = 4$ is lower than that of the neighboring cluster sizes and thus cannot be the reason for the special stability.

Sustained off-resonance irradiation collision-induced dissociation (SORI CID) experiments performed in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) reveal, that the loss of neutral clusters $(NaCl)_x$ with even $x$ (especially $x = 2$ and $x = 4$) is in most cases more favorable than the loss of single NaCl units, as assumed so far [2]. This can be explained by the calculated high stability of neutral clusters $(NaCl)_x$ with even $x$, whose minimum energy structures are cubic, resembling the sodium chloride crystal lattice.

Analysis of the density of states as well as the Rice-Ramsperger-Kassel-Marcus (RRKM) rates for the anionic and cationic magic cluster with $x = 4$ and the neighboring cluster sizes with $x = 3$ and $x = 5$ yields an explanation for the high stability of the smallest magic clusters. Our findings emphasize the importance of considering the kinetics of the cluster dissociation, not only the respective energetics.

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# Machine learning interatomic potentials for molecular crystals

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Molecular crystals are a common and important class of crystalline materials. However, modeling molecular crystals based on first principles (eg. with density functional theory) is often difficult due to the size of a typical unit cell. Machine learning interatomic potentials offer a way to bring density functional theory accuracy to the length and time scales needed for modeling molecular crystals. Due to the need for an accurate description of both intramolecular and intermolecular forces, such potentials are not easy to construct. On the other hand, since molecular crystals are composed of only a handful of elements (C, H, N, O, ...) it should be possible to construct a general interatomic potential valid for any crystal. In principle, to train machine learning potential one would need to create a sufficiently large database of molecular crystals calculated with the desired accuracy. This is also a very challenging task. In this talk, I will show how to partially avoid this step using transfer learning and existing databases of accurate calculations for small molecules.

# Universal pairwise interatomic van der Waals potentials from quantum Drude oscillators

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Noncovalent van der Waals (vdW) interactions play an essential role in molecules and materials, being one of the driving forces that determine the structure and stability of (bio)polymers. Classical force fields, which remain the most used approach in simulations of such large and complex systems, still mostly rely on empirical Lennard-Jones (LJ) description of vdW interactions. However, LJ potentials usually underestimate the equilibrium vdW energy and severely overestimate the asymptotic $C_6$ coefficients [1]. In addition, parametrization of the LJ potential is not a unique and universal procedure for all chemical elements, and it might significantly vary depending on the particular problem addressed [2]. Therefore, universal and accurate yet efficient and scalable quantum-mechanical vdW potentials are strongly desired. Here, we use a coarse-grained physical model of electronic response – quantum Drude oscillator (QDO) [3, 4] – to derive analytical pairwise vdW potential between atoms, which depend just on two *non-bonded* atomic parameters: static dipole polarizability $\alpha_1$ and dispersion coefficient $C_6$. This makes our potential universal, i.e. applicable to all chemical elements. Our vdW-QDO potential derived for noble-gas dimers shows excellent accuracy against state-of-the-art *ab initio* and analytical methods. In addition, we demonstrate that the shape of our vdW-QDO potential can accurately describe group II metal dimers. For these highly polarizable systems, we need to introduce the damping function for dispersion energy, which we derive consistently within the QDO model. Finally, we apply vdW-QDO potential (in combination with atom-in-molecule approach [5]) to dispersion-dominated molecular dimers from the S66×8 dataset [6]. We show that our method delivers accurate approximation to the SAPT dispersion energy curves of those molecules, whereas the SAPT exchange energy is recovered less accurately. The latter indicates that exchange-repulsion between molecules requires a more general (many-body) treatment, beyond the conventional pairwise-additive approach.

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# Non-covalent interactions in semiempirical QM methods: from simple corrections to machine learning

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Semiempirical quantum-mechanical (SQM) methods are computational chemistry methods combining proper quantum-mechanical description of molecular systems with approximations that offer enormous increase of computational efficiency compared to more complex *ab initio* quantum mechanical or DFT methods. In the past decade, we have worked on improving the description of non-covalent interactions (NCI) in SQM methods. It is a prerequisite for work with large molecular systems where NCI play a crucial role. Our ultimate goal is to apply these methods to biomolecules, with potential practical applications in computer-aided drug design. We pioneered the corrections for hydrogen and halogen bonds, and together with a correction for London dispersion, and the latest method in this series, PM6-D3H4X, is one of the top contenders in the field.[1]

Despite these successes, our extensive work with SQM methods also revealed their limitations. These issues are of course connected with the approximate nature of the SQM methods, but they seem to be hard to address by either modifying the formulation of the SQM method (without loosing its efficiency) or by adding simple *a posteriori* corrections. The most important unsolved issues are non-covalent interactions at short range, and the description of conformation energies.[2]

Recently, we built a machine learning model serving as a correction for PM6 and trained it on an extensive database including the Non-Covalent Interactions Atlas data sets.[3] The resulting PM6-ML method[4] is able to correct all the remaining issues noted above, and it clearly outperforms all previous SQM methods in an extensive set of validation data sets covering different phenomena. In comparison to the previous attempts in this direction, PM6-ML covers larger chemical space what makes it applicable e.g. computer-aided drug design, and takes an advantage of a linear-scaling implementation of the SQM calculation what allows working with systems with thousands of atoms.

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# APPLICATIONS OF THE THEORY OF INTERMOLECULAR INTERACTIONS IN THE RATIONAL DESIGN OF INHIBITORS AND CATALYSTS

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Numerous specific properties of molecular aggregates are governed by intermolecular interactions, the accurate description of which is the key to model binding of ligands or substrates to proteins and use it in drug or biocatalyst design. Interactions involved are sometimes too strong to apply perturbational methods. This could be circumvented by application of Hybrid Variation-Perturbation Theory [1-2], yielding electrostatic multipole, electrostatic penetration, exchange, delocalization and correlation terms numerically almost identical with corresponding components defined within SAPT [3]. Some of these terms could be represented by corresponding atom-atom potentials [4-6], allowing analysis of the physical nature of interactions and derivation of hierarchies of simpler non-empirical methods applicable for large molecular aggregates involved in drug [6] or catalyst design [2,7], exploration of sources of extreme catalytic activity of enzymes with hydrogen bond chains in active site [8], verification of alternative enzyme reaction mechanism variants [9] or examination of the covalent nature of interactions [10].

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# Force Field Analysis Software and Tools (FFAST)

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The introduction of machine learning (ML) models has a strong impact in the field of atomistic simulations. When trained on accurate computational chemistry methods such as density functional or coupled cluster calculations, ML techniques enable studying large-scale systems at realistic conditions. Myriads of applications have already proven the ability of ML models based on ab initio reference data to reproduce complex processes in liquids, solids, or gases. Nevertheless, it is essential to remember that ML models also contain strong assumptions that limit their applicability range. Therefore, analyzing ML predictions' and identifying possible pitfalls becomes imperative when pushing simulations to their limits in targeting complex problems. In my talk, I will introduce a novel software package, FFAST, enabling this analysis intuitively and interactively. Compatible with most of the modern ML architectures such as Nequip, sGDML, SchNetPack, Allegro, and GAP, to name a few examples, FFAST combines unsupervised and supervised techniques providing a swiss-knife tool for comparison, accuracy analyses, and visualization of ML models. The baseline features of FFAST include the following:

- Distributions (of errors) on energy and force predictions available for multiple dataset/model combinations;

- Clustering techniques provide a way to find problematic configurational space regions or split the dataset into subsets.

- Scatter plots to find outliers quickly;

- The distribution of atomic (mis)predictions to determine the difference in (predictions) behavior between chosen elements.

The user can zoom in on most plots and choose to create sub-datasets for further analyses. Subsets and datasets can be saved in multiple formats if external editing or investigation is needed. In addition, the program comes equipped with a 3D visualization tool that can work with dozens of thousands of atoms providing further interactive analyses.

# Symmetry-Adapted Perturbation Theory Based on Multiconfigurational Wave Function Description of Monomers

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We introduce a formulation of the symmetry-adapted perturbation theory (SAPT) based on multiconfigurational (MC) wave-function description of the monomers [1]. The method is designed to handle noncovalent interactions between systems that necessitate a multiconfigurational treatment. It proves particularly useful when dealing with strongly correlated molecules or electronically excited states. SAPT(MC) utilizes one- and two-particle reduced density matrices of the monomers and employs the single-exchange approximation to account for exchange energy contributions. To obtain second-order terms, response properties from extended random phase approximation (ERPA) are incorporated. The dispersion components of SAPT(MC) have been introduced in our previous works [2, 3]. Additionally, the method can benefit the Cholesky decomposition of two-electron integrals. We discuss the performance of SAPT(MC) combined either with generalized valence bond perfect pairing (GVB-PP) or with complete active space self-consistent field (CASSCF) wave functions. We explore the possibility of accounting for electron correlation effects within the monomers using range-separated MC density functional theory [4].

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# High-Order Many-Body Expansions Via a Bottom-Up Approach

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The many-body expansion provides an attractive way to extend electronic structure calculations to large systems, and forms the basis of a wide variety of fragment-based approximations in quantum chemistry [1]. For systems of polar monomers, many-body induction effects are significant and questions have been raised regarding when the many-body expansion (of monomers, dimers, trimers, etc.) may be truncated [2], an issue that is complicated by the fact that basis-set superposition error can masquerade as high-order induction [3, 4, 5]. To address these questions, we have implemented the many-body expansion using a novel "bottom-up" algorithm that incorporates on-the-fly energy-based screening [6] of the $n$-body interactions at a semi-empirical level of theory. Screening eliminates nodes on the graph-theoretical representation of the subsystems as it is constructed, thereby minimizing the number of high-level electronic structure calculations that is required. This allows us to extend high-order many-body expansions to systems of unprecedented size, $e.g.$, up to $n = 7$ for $(H_2O)_{64}$, conquering what has recently been suggested [7] to be intractable combinatorics for $n > 4$. Results with both correlated wave function models and density functional theory shed light on the nature of many-body induction effects in the latter, and how they are affected by delocalization error, and furthermore clarifies the role of basis-set superposition error within the many-body expansion. An open-source software framework to perform these calculations will also be described.

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# Anharmonic Vibrational Frequencies of Non-Covalently Bound Systems via Vibrational Perturbation Theory

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

Herein, we assess the quality of VPT2 calculations for a diverse set of small molecular dimers, which are held together by van-der-Waals dispersion interactions alone or also by intermolecular hydrogen bonds. To accurately capture all intermolecular interactions, we first utilize CCSD(T) for the whole set of dimers. Our so obtained VPT2 results are compared with available experimental data or high-level calculations of potential-energy surfaces. Problematic large-amplitude motions [2] like inter-/intramolecular rotations are described by one-dimensional hindered rotor models. Furthermore, we also discuss the accuracy of a simpler approach utilizing Morse oscillators. Later on, such an anharmonic approach can also be utilized for molecular crystals either in a fully periodic way or by embedding anharmonic monomer and dimer calculations into harmonic periodic calculations in a similar fashion as currently done for energies and geometries [4, 5]. This might be crucial for complicated crystal structure predictions, where numerous energetically similar polymorphs have to be ranked according to their Gibbs free energy [6].

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# Abstracts: Posters

# Properties of Isolated Small Molecules, Molecular Ions and Molecular Clusters - Theory vs. Experiment

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Calculated properties of isolated small molecules, molecular ions and molecular clusters in their electronic ground state, like equilibrium structure ($r_e$ structure) and fundamental frequencies, compare very well with experimental data (for the latter see [1, 2] and references therein), if these properties are calculated at sufficiently high level of theory (e. g. with an explicitly correlated coupled-cluster method like CCSD(T)-F12). For systems composed of up to, say, five or six light atoms ($Z \leq 10$), sub-pm errors in bond lengths, few degrees errors in bond angles and few percent errors in fundamental mode frequencies can be achieved, even in cases with degenerate electronic ground state terms.

For systems composed of heavier atoms ($Z > 10$), where relativistic effects (scalar effects as well as spin-orbit coupling effects) are important, the situation is much less clear. Systematically improved all-electron calculations become unfeasible rather quickly. Data for selected systems will be presented to discuss the state of affairs.

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# P2

52

# From micro-solvation to solvation: Study of the interaction between pesticides and water

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A large number of pesticides are authorised in the European Union and are used in agriculture. A better understanding of pesticides requires the study of their behaviour and fate in the environment (soil, water and air). This is a major challenge in order to limit their harmful impact on the environment. The global project in which my thesis subject is included follows a step-by-step approach to explore the interactions between a pesticide and the various components of a soil that can be modelled at the atomic scale. Thus, I am studying the micro-hydration[1] of two pesticides, fenhexamid (N-(2,3dichloro-4-hydroxyphenyl)-1-methylcyclohexanecarboxamid) and metamitron (4-amino-3-methyl-6-phenyl-1,2,4-trizan-5-one), which are respectively a fungicide and an herbicide. The first results and the method used will be presented. First, in molecular dynamics with a DFTB potential, we exhaustively explore the potential energy surfaces of the pesticide-$(H_2O)_i$ systems for $i$ = 1-20. Along these trajectories, we select n structures that we optimise in DFTB. Among these minima, the n energy-lowest ones are re-optimised in DFT (PBE, B3LYP). The relative energies of the different minima, the interaction, complexation and deformation energies are calculated. Basis effects are studied by comparing the results obtained with a double ζ (+polarisation) basis, 6-31G\*\*, with a triple ζ (+polarization +diffuse) basis, 6-311+G(2d,2p). Basis set superposition errors were taken into account using the counterpoise method. In addition, the effects of dispersion are evaluated looking at the impact on the different energies of the empirical corrections of S. Grimme (D2 and D3).
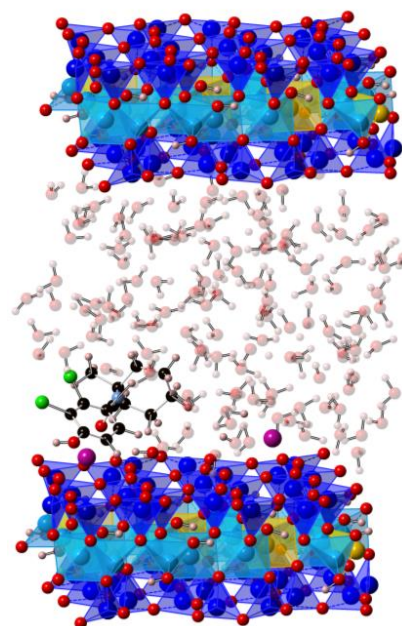


**Figure 1.  Representation of the hydrated metamitron-(Ca- Montmorillonite) system.**

**Keywords:** micro-solvation, pesticide, DFT, DFTB, Molecular Dynamics

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# Energy Barriers of Polymorphic Transitions via First-Principles Nudged Elastic Band Calculations

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Molecular crystals represent versatile materials that are used in the pharmaceutical industry, agriculture, and as explosives. The existence of molecular crystal polymorphs with similar energies complicates modelling of such systems, nevertheless the study of their thermodynamic stabilities achieved remarkable results for molecular crystal structure predictions. [1, 2] However, kinetic properties of transitions between polymorphs remain much less understood. Until now, energy barriers of transitions between molecular crystals polymorphs have been mostly assessed with the help of force-field molecular dynamics simulations. [3, 4] Here, we present an alternative approach, based on the combination of first principles methods with a solid-state nudged elastic band (NEB) approach [5], which allows fully periodic NEB calculations with varying unit-cell parameters. We examine the feasibility of this method by applying it first to simple test cases using molecular crystals made out of small rigid molecules with similar unit cells. Specifically, we present PBE+MBD and PBE0+MBD energy barriers of one polymorphic transition for 1,4-diiodobenzene and oxalic acid dihydrate, respectively.

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# Assessing Density Functional Methods for Accurate Michael Acceptor Affinities of Lewis Base Catalyzed Reactions

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Lewis base (LB) catalysis presents an invaluable tool in synthetic chemistry, where a key-step of many important transformations involves the formation of zwitterionic intermediates constituted of the LB catalyst and a Michael acceptor (MA) [1, 2]. Over the past, several scales have been employed as a measure for the reactivity of a LB, such as the recently introduced Michael Acceptor Affinity (MAA), i.e., the negative Gibbs free energy of the reaction of a LB with a MA [3, 4, 5]. Thus, to accurately predict such measures, the development of appropriate computational protocols is of vital importance for the succesful implementation of novel organocatalysts.

Here, we present a cheap yet accurate computational procedure for the calculation of zwitterionic species obtained by evaluating the performance of 22 density functional approximations (DFAs) regarding geometries and Gibbs free energies on a benchmark set of 36 zwitterions against MP2/CBS+$\Delta$DLPNO-CCSD(T) [6]. By employing our method for the calculation of MAAs to an extended dataset a good qualitative estimate of the experimentally observed activity trends of various LBs and MAs could be obtained. Compared to other commonly used scales (e.g., Methyl Cation Affinities, MCA), MAAs were found to present a significant improvement in the prediction of catalyst activity, especially when sterically congested LBs and/or MAs are involved.

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# Understanding exchange-repulsion with orbital contributions

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We provide evidence that the repulsive contribution (exchange-repulsion) to the interaction energy of molecules can be decisive for aggregates and crystal structures. Modelling the repulsive part of intermolecular interactions with molecular orbitals leads to a pictorial explanation for stable arrangements of non-covalently bound molecular complexes.[1] For example, the proposed model is able to explain the parallel displaced crystal structure of benzene-hexafluorobenzene, which cannot be rationalized otherwise.[2] The main idea of the model is to attribute the exchange-repulsion energy to the overlap of the occupied molecular orbitals of the individual molecules. Specifically, significant overlap leads to repulsion, while zero overlap leads to (little) attraction.

Our work is based on the intermolecular perturbation theory developed by Hayes and Stone [3] and the equation for the exchange-repulsion energy derived by Jensen and Gordon [4]. Using further approximations, canonical Hartree-Fock-orbitals, which are generally non-orthogonal, we have derived a formula that expresses the exchange-repulsion in terms of orbital-orbital contributions. Our equation is asymptotically identical to the SAPT result for the exchange-repulsion. With this method, the role of each orbital can be identified. The procedure is illustrated using the example of $N_2$-Ne, as it is suitable due to the small number of orbitals. However, we indicate that the model is also applicable to larger systems such as halogen-bonds or $\pi$-$\pi$-interactions, like the benzene-hexafluorobenzene system mentioned above.

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# Computational study of the dissociation reactions of methyl acrylate on the Cu(111) surface

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Biodiesel has emerged as an important renewable transportation fuel, and it is considered frequently promising as a sustainable alternative. This biomass-based fuel comprises long-chain alkyl esters with relevant double-bond unsaturation that provides a significant influence on their physical properties and well-known poor combustion characteristics[1]. In biodiesel, besides oxidation reactions, thermal decompositions can also appear during combustion, and their products can be corrosive to the metal surfaces of an engine. Thermal decompositions are unimolecular complex dissociations, and as in other fuels, surrogate molecules achieve a better understanding of such mechanisms in biodiesel[2]. In this study, we are interested in monitoring the elementary dissociation dynamics of non-branched unsaturated methyl ester surrogates such as methyl acrilate, in conjunction with the corrosion that the reaction products induce on metal surfaces, both systems in the absence of air.

We will present the results of a computational DFT study on the microscopic mechanisms involved in the adsorption and dissociation of methyl acrylate on the Cu(111) surface. Of special interest is the analysis of important differences with the unimolecular decomposition in the gas phase which has been studied experimentally and theoretically[3]. As expected the thermochemistry and activation barriers change drastically indicating the catalytic effect of the surface. Technical details associated with different methodologies[4,5] will also be presented.

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# Molecular oxygen trimer: when usually small effects become crucial

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There have been very few detailed experimental or theoretical studies of molecular oxygen clusters beyond the dimer[1,2,3,4,5]. The only exceptions are a Stern-Gerlach study[6] and experimental studies on their anionic forms[7]. Most experimental studies of clusters have relied on infra-red spectroscopy which of course is not applicable in this case. From the theoretical point of view oxygen clusters present various challenges given the open-shell nature of the monomer as well as having low-lying electronic states.

In this work we present a detailed theoretical study of the molecular oxygen trimer where the potential energy surface of the seven multiplet states have been calculated by means of a pair approximation with very accurate dimer ab initio potentials[4]. In order to obtain all the states a matrix representation of the potential using the uncoupled representation has been applied. The $S=0$ and $S=1$ states are nearly degenerate and few isomers appear for most multiplicities.

A crucial point in deciding the relative stabilities is the zero-point energy which represents a sizable fraction of the electronic well-depth. Therefore we have performed accurate diffusion Monte Carlo studies[8] of the lowest state in each multiplicity. Analysis of the wavefunction allows a deeper interpretation of the cluster structures. Finally we also estimate the relevance of three-body effects using accurate ab initio methods.

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# Generalized perturbative orbital relaxation correction based on random phase approximation

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Inspired from variationally-minimized generalized Kohn-Sham semicanonical projected random phase approximation (GKS-spRPA), we formulate a generalized scheme for perturbative orbital relaxation corrections. One case of such corrections (RPASingles or RPAS) includes relaxation- correlation effects via a screened RPA orbital rotation gradient. It includes the orbital relaxation effect in an iterative-free manner, which reduces the cost by a factor of number of orbital optimization steps.

Using RPAS, we observe that such relaxation-correlation effects may be required to predict (a) correct equillibrium geometries and correct short-range behaviour for intermolecular interactions, and (b) accurate spin gaps and correct ground spin state for transition metal complexes.

# The importance of being anharmonic: the binary system methanol-benzene

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This study discusses the importance of anharmonicity for the description of thermodynamic properties on the binary system methanol-benzene at molecular level. The binary mixture methanol-benzene is particularly interesting because it forms an azeotrope at x(MeOH) = 0.61 and 58.3°C. In this work, we present molecular clusters that describe the pure solvents methanol and benzene as well as the mixture in a composition range x(MeOH) = 0.0 – 1.0. [1] For the azeotrope, a possible structure was proposed by Perchard [2] consisting of two benzene and three methanol molecules, with was also included in this work.

For the mixed dimer, the anharmonicity is characterized in detail for different types of vibrational modes: the intermolecular O-H···benzene stretching, the benzene deformation and the methanol libration.[3]

Further, the vibrational entropy was computed for all molecular clusters of the binary system methanol-benzene using harmonic, RRHO corrected harmonic, scaled harmonic and anharmonic frequencies. From these data, the effect of the anharmonicity is discussed and compared to literature data.

From the thermodynamic data, cluster populations as well as the boiling point diagram are extracted via the quantum cluster equilibrium method using the Peacemaker program. [4]

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# Nuclear Electric Resonance for Spatially-Resolved Spin Control in Molecular Systems

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Nuclear electric resonance (NER) has been subject to scientific research as an alternative to common magnetic control mechanisms such as nuclear magnetic resonance. The technique exploits the coupling of radiofrequency electric fields with the total spin of the respective nucleus, mediated by the electric field gradient generated by the electronic surrounding of the nucleus. Compared to magnetic fields, electric fields or local electron density fluctuations caused by changes in the atomic environment provide a much higher spatial resolution for the addressing of specific nuclear spins of a molecular system. Within this context, the phenomenon of nuclear quadrupole resonance is investigated as a potential tool for coherent spin control in molecular systems.

We study the impact of the molecular environment and of external electromagnetic fields on the electric field gradient of atomic centers with suitable nuclear spin configurations. We derive an abstract description of time-dependent nuclear quadrupole resonance from quantum mechanical principles that entails commonly applied approximations and offers insight into the structure of coherent nuclear quadrupole resonance. Due to its spatial confinement NER is a promising candidate for scaling up nuclear-spin-based quantum devices. By relying on electric fields, it may be possible to achieve a level of precision and control that was previously unattainable through magnetic resonance alone.

# Fragment-based *Ab Initio* Molecular Simulation and Machine Learning for Designing Interactions in CO₂-physisorbing Liquids

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To achieve the targets set in the Paris Agreement, global $CO_2$ emissions must be reduced by 7.6% annually over the next decade. [1] This requires the effective use of carbon capture and storage (CCS) technologies. However, one of the barriers to the use of such systems is their absorption phase. Carbon capture costs are primarily influenced by the energy required for solvent regeneration, which is directly related to $CO_2$–solvent interactions and the separation efficiency from other gases. Improving the efficiency lowers the carbon capture cost, facilitating the use of CCS technologies.

With this background, developing efficient and sustainable $CO_2$-absorbing liquids has received immense attention in chemical engineering and related fields. [2] While there are several types of $CO_2$ absorbers, the intensive study of ionic liquids (ILs; room-temperature molten salts) and deep eutectic solvents (DESs; hydrogen-bonded mixtures in a broad sense) would give basic science contributing to environmental engineering toward the development of a safe and sustainable society. They are highly stable (low volatility and highly heat resistant) and can be chemically designed various cation/anion or hydrogen-bonding-donor/acceptor combinations.

A significant limitation of developing physical absorbents (those not leading the $CO_2$ chemisorption) for applications is the combinatorial explosion of the ionic or molecular species. This study aimed to explore highly $CO_2$-selective absorbents from 402,114 IL and 1,533,528 DES candidates by using the *ab initio* statistical thermodynamics theory and materials informatics approaches. [3-5]

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# Computational Study of Adsorption of CO and HF on a NiF$_2$ Surface Model

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Fluorinated organic compounds are essential in modern day to day life and, therefore, understanding their efficient synthetic pathways is of great importance. Electrochemical fluorination on nickel anode (the Simons process) [1] is an important industrial way for produccuing fluorinated organic compounds. Even though it has been around since the middle of the last century its mechanism is not completely understood. The commonly accepted mechanism is believed to proceed in two stages; (1) formation of Ni$_x$F$_y$ film on nickel anode immersed in anhydrous hydrogen fluoride under applied external potential and (2) fluorination of the substrate mediated by high valent Ni species formed on the anode. The first step of this mechanism has been investigated by our group [2, 3], however no investigations on the second step have been reported before.

The twice oxidised (001) NiF$_2$ surface, where the surface nickel atoms are in formal +4 oxidation state, has been identified as the simplest system to model fluorination reactions happening in the Simons process. Furthermore, this surface shows an [F$_2$]$^-$ moiety which could be a readily available fluorine source. Therefore, we have chosen to investigate the fluorination of CO on this surface with the special emphasis on the influence the co-adsorbed HF molecules have on the catalytic reaction.

All the calculations were done by means of periodic, spin unrestricted DFT, within the framework of PBE+U/D3 approach. As first step adsorption of the single CO molecule on the twice oxidised (001) NiF$_2$ surface was studied. To account for the more realistic experimental situation, where the solvent is hydrogen fluoride, we explicitly co-adsorbed some hydrogen fluoride molecules on the surfaces. This way we were able to get various adsorbed structures, including COF$_2$ and CF$_3$OH. For selected transformations we have investigated the reaction profiles by CI-NEB. Furtheremore, to approach the liquid HF phase, we added layers of HF molecules and searched for the energy minima by means of *ab-initio* molecular dynamics (AIMD).

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# Importance of Trimer Interactions for the Description of Molecular Crystals via Multimer Embedding

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The ability to accurately describe molecular crystals by computational methods is highly important for the pharmaceutical industry and the field of crystal structure prediction (CSP), as different polymorphs of the same compound typically differ in their lattice energies by only a few kJ/mol. However, computational methods that reach such accuracies (e.g. density functional theory (DFT) using hybrid functionals) require enormous amounts of computational time and memory, potentially exceeding even the capacities of modern HPC facilities for larger systems. One option to reduce the necessary computational resources, while still keeping the required level of accuracy, is the usage of embedding methods, such as the subtractive scheme introduced in Ref. 1. We recently introduced an implementation of this embedding scheme, wherein we embed multimers at the PBE0+MBD level into the periodic calculation at the PBE+MBD level. [2] For the energy, multimers up to trimers are embedded, while for the calculation of the atomic forces, stress tensor, and harmonic frequencies up to dimers are used.

Herein, we further extend our embedding approach to also incorporate trimer interactions for the calculation of the atomic forces, stress tensor, and harmonic frequencies. Specifically, we present initial results of this trimer embedding for a subset of the X23 benchmark set for molecular crystals. We show that, for this subset, the inclusion of trimers indeed further improves the resulting cell volumes.

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# P14

## Development of computationally friendly procedures for solid-state organic cohesion modelling

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Due to the existence of attractive and repulsive forces between specific functional groups and molecular fragments, certain characteristic arrangements of molecules in the crystal, reflecting these forces are also preferred. Different crystal structures of the same substance, i. e. polymorphs, exhibit different physicochemical properties. Active pharmaceutical ingredients (APIs) often exhibit polymorphism, which makes their development considerably more expensive and time-consuming. At the same time, the development of computational and predictive methods, together with the increased availability of computational capacity, allows the prediction of crystal properties *in silico*, thus circumventing some of the lengthy experiments [1].

Quantum-chemical calculations for the solid state usually rely on electron density functional theory (DFT), which provides reasonably good accuracy [2]. Nevertheless, these DFT methods are still too expensive for complex molecular crystals, justifying the effort to find some balance between the desired accuracy and computational cost. Semi-empirical methods based on the density functional tight binding (DFTB) method could provide a good and computationally relatively inexpensive tool with respect to DFT calculations at least for high-throughput scanning of crystal energy landscapes. Calculations of both vibrational states and electron energy is an important step towards predicting the thermodynamically preferred polymorphic form. It is also important to account for the anharmonicity of vibrations in crystals for a reasonable assessment of the relative thermodynamic stability of polymorphs. This is partly captured by the quasi-harmonic approximation [3], which takes the energy of vibration relative to the volume of the crystal. This often involves calculations of many thousands of perturbed structures to evaluate the forces acting on each symmetrically non-equivalent atom. The lower cost of DFTB methods is thus beneficial.

For several API crystals, a study comparing the accuracy of DFT and DFTB calculations for molecular crystals is presented. DFT calculations are performed at the PBE-D3/PAW level of theory implemented in the VASP code, while DFTB3 methods with the D4 dispersion correction and the 3OB parametrization as implemented in the DFTB+ code are used. Both methods are used in the same way to follow the quasi-harmonic models of crystal cohesion. The main goal of this procedure is to find an efficient and reliable combination of DFTB and DFT methods for each computational step in the quasi-harmonic approximation. This computational approach is then validated by comparison with reference experimental and DFT data. This allows to efficiently rank polymorphs even for larger molecules in terms of their Gibbs energies at finite temperatures [4].

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# Extensive Benchmark DFT-SAPT Data Processing Reveals New Aspects

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Symmetry adapted perturbation theory based on density functional theory, DFT-SAPT or sometimes called SAPT(DFT), has the potential to give accurate results for intermolecular interactions besides a favorable computational scaling with system size [1]. However, in terms of both the non-covalent interaction (NCI) characteristics and the choice of exchange-correlation (xc) potential with or without single exchange ($S^2$) approximation, different levels of accuracy can be achieved.

We extrapolated DFT-SAPT to the complete basis set limit for 19,293 dimer structures involving 2312 potential curves [2]. With taking the data related to different xc potentials, $S^2$ or $S^\infty$ exchange expansions, and charge transfer energies into account, the total number of generated data amounts to around 350 k quantum chemical interaction energy values for a variety of NCIs. The results reveal that the $S^2$ approximation and B3LYP-AC potential mostly outperform $S^\infty$ and PBE0-AC, respectively. The reasons are likely error cancellation effects between the approximate exchange expansion and the non-exact xc potential. From the energy decomposition aspect, large charge transfer energies together with the existence of heavy atoms in the monomers turn out to be the source of large errors in many DFT-SAPT calculations. Dispersion-dominated systems and weak hydrogen bonds are treated rather well by DFT-SAPT. The dispersion energy tends to decay w.r.t the monomer separations mainly as $R^{-6}$ in these systems while the same is not true for other NCIs such as e. g. $\sigma$-hole interactions. Finally, a reduced data set with the lowest redundancy and the highest coverage is introduced as a good representation [3].

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# Improvement of DFTB parameters toward halogen bonding interaction in drug discovery

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Halogen bonding interactions have been applied for drug discovery with fewer side effects since they are higher-directional than hydrogen bonding interactions. For example, Cathepsin L inhibitors used for cancer treatment can increase a ligand's activity by forming halogen bonding interactions between an iodine atom and the target protein.[1] Since the physicochemical origin of the strong anisotropy is the exchange-repulsion term,[2] quantum chemical calculation with a low computational cost is required for their quantitative description.

With the backgrounds, we tried to improve the accuracy of the Density Functional based Tight-Binding method (DFTB). [3] Before large-scale applications, we evaluated the accuracy of the modified DFTB parameters with small biomolecular model systems. First, the structures of mono-substituted halomethanes and halobenzenes in the gas phase were evaluated by DFTB and PBE-D3/aug-cc-pVDZ(halogen atom: MCP-ADZP). Intermolecular interaction potentials were analyzed hereafter between amino acid-trimers and halobenzenes (see Figure). As a result, it was found that our modified DFTB parameters can describe the halogen bonding interactions at a higher level than default parameters. In this session, we also discuss the electronic state of biomolecular systems using modified DFTB parameters. [4]
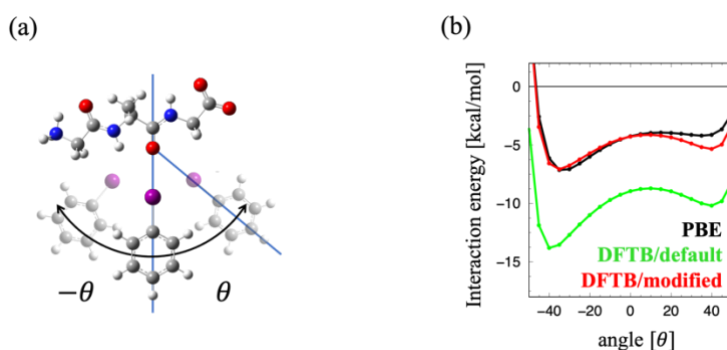


Fig. (a) The image of interaction and the definition of interaction angle,
(b) Interaction potentials between amino acid-trimers and iodobenzene.

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# Assessment of random phase approximation with different exchange-correlation functionals for description of binding energies of molecular solids

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Reliable prediction of the structure and stability of molecular solids is considered one of the important keys to explore the numerous applications of these systems. However, the need to describe reliably electron correlations in solids makes the accurate calculations of their binding energies challenging. Moreover, the relative energies of different phases or polymorphs of molecular solids are often small, leading to high requirements not only on the accuracy but also on the precision of the numerical set-up. To date, the calculations of binding energies for molecular solids with many atoms can become prohibitively expensive for high levels of theory, such as coupled clusters with singles, doubles, and perturbative triples (CCSD(T)). In this study, we assess the accuracy of a simpler and computationally cheaper method (random phase approximation (RPA)) based on different exchange-correlation functionals (PBE, SCAN, PBE0, and SCAN0) by comparing with CCSD(T) reference data. To do this, we calculated dimer, trimer, and tetramer contributions at the RPA and CCSD(T) levels using many-body expansion (MBE) approach for four crystalline hydrocarbons: ethane, ethene, and cubic and orthorhombic forms of acetylene. We find that the choice of the DFT functional affects significantly the results of the many-body contributions, but the total binding energies are found to be similar for PBE and SCAN, and for PBE0 and SCAN0. In addition, when Hartree-Fock (HF) exchange is added to PBE and SCAN, the energy changes of all many-body contributions are larger for PBE than for SCAN. Finally, while the calculations are more computationally expensive for PBE0 and SCAN0 than for PBE and SCAN, the RPA method with renormalized singles energy (RSE) corrections based on PBE and SCAN performs better than that based on PBE0 and SCAN0 for all the considered systems.

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# P18

# Spin- and charge reorganization during forming and breaking of covalent bonds

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The traditional explanation of covalent bonding is based on Lewis' electron pairs, the Heitler-London wave function and doubly occupied bonding MOs are two quantum chemical models used to support e Lewis' view. Multiple bonds are represented my a corresponding number of Heitler-London wave functions or doubly occupied bonding MOs. No convincing explanation is given when two reactants in low-spin states are assumed to form multiple bonds during a chemical reaction. OVB (orthogonal valence bond theory) can do this.[1-3] The dissociation reactions of $C_2H_4$ and $Si_2H_4$ are studied in different symmetries. It is claimed that OVB CSFs describe diabatic states.

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# Orbital Contributions to the Exchange-repulsion Energy in Donor- Acceptor Systems

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We propose that the exchange-repulsion energy $E_{exr}$ plays a crucial role for the arrangement of molecules in crystals and aggregates of organic donor-acceptor (DA) systems. Furthermore, we present a pictorial explanation for the preferred DA structures based on the canonical molecular orbitals [1] which is an extension in line with prior considerations of orbitals on aggregate structures [2].

Organic donor-acceptor systems are particularly interesting with ample applications for ferroelectrics, field effect transistors, light-emitting diodes, and organic photovoltaics. Particularly noteworthy are enormous electric conductivities observed for tetrathiofulvalene-tetracyanobenzoquinodimethane (TTF-TCNQ) co-crystals. The most common model for the arrangement of organic $\pi$-systems proposed by Hunter and Sanders [3] states that aggregate structures are mainly determined by the electrostatic energy and in particular by quadrupole-quadrupole interactions. We show that it does not apply for the investigated molecules at the small separating distance ranges found in crystal structures.

Three DA systems are considered; the first one is the combination of benzene and tetracyanoethylene (TCNE). TCNE has a high electron affinity localized on the double bond (due the cyanide groups that attract the electrons from the double bond), while benzene is an electron donor molecule with a high electron density in its $\pi$ electron system. When these two molecules are brought into contact, a partial electron transfer can occur from the benzene to the TCNE molecule and a DA complex is formed. The second system is benzene-benzoquinone and the third one is TTF-TCNQ.

SAPT0/jun-cc-pVDZ level of theory was used to calculate and to decompose the total interaction energy into electrostatic energy, exchange repulsion, induction energy, dispersion energy, and charge transfer energy. The method proposed in Ref. [1] is used to obtain orbital contributions to the exchange-repulsion energy.

In the benzene-TCNE complex, the equilibrium structure was found for a distance of 3.0 Å between the molecular planes where the TCNE molecule is located on top of the benzene molecule. The same is found for the TTF-TCNQ system. This stacking mode is commonly referred to as the parallel-stacked, sandwich, or eclipsed arrangement. For the benzene-benzoquinone complex a parallel-displaced (slip-stacked) arrangement is found to be most favorable. These observations are explained by molecular orbital contributions (MO) to the exchange-repulsion energy, in particular due to the $\pi$-$\pi$ contributions of the donor and acceptor molecules.

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# TDDFT Investigation on a Perylene-based Logic Gate for Nitric Oxide Sensing

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Nitric oxide in the endothelium is a critical molecule for regulating vascular function as well as a key predictor of endothelial dysfunction [1] which is notorious for being an important contributor to the progression of atherosclerosis [2], consequently leading to a variety of complications most notably the world's leading cause of death – Coronary Artery Disease (CAD) or Ischemic heart disease as reported by the World Health Organization [3]. Researchers from LOGICLAB (Molecular logic lab-on-a-vesicle for intracellular diagnostics) - Innovative Training Network have designed and synthesized a tailor-made nitric oxide sensing compound for this purpose. In this presentation, we will shed light on the mechanism of this novel Perylene-based logic sensor for the detection of nitric oxide, give insights on ways to enhance its efficiency and tackle its use as an annihilator for triplet–triplet annihilation - upconversion (TTA-UC). Time-dependent density functional theory (TDDFT) methods are employed to decipher the electronic structure of the sensor and the synergy between theory and experiment will be demonstrated.

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# PyConSolv:

# A Python Package for Conformer Generation of (Metal-Containing) Systems in Explicit Solvent

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PyConSolv is a freely available python package that automates the generation of conformers of metal and non-metal containing complexes in explicit solvent, through classical molecular dynamics simulations.[1] This allows one to obtain more realistic structures when dealing with systems whose structure heavily depends on the presence of solvent, such as supramolecular cages.[2]

A streamlined workflow greatly facilitates rapid generation of parameters for transition metal systems, requiring minimal input from the end user. This is provided in the form of a structure (XMOL format) and details about the quantum mechanical methods to be used, as well as solvent. Additionally, the package can also account for charged systems by including arbitrary counterions.

The force field parameters are determined based on the bonded model approach, by interfacing with the AmberTools, ORCA, and Multiwfn software packages. The system is then solvated, with either one of the 18 pre-parametrized solvents or one provided by the user, and equilibrated. Following a cMD production run, the trajectory is clustered and the individual cluster representatives are ranked according to their relative energy, based on single point energy calculations.

We demonstrate the applicability of our package on a number of (transition-metal-containing) systems. The software is provided open-source and free of charge on github[3] and pypi.

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# A fragment-based approach for cohesion energy of crystalline ionic liquids: Doing it right

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Accurate prediction of thermodynamic properties of crystalline phases remains a vital goal of theoretical studies. Much more so when the available experimental data exhibit wild inconsistencies or are outright contradictory. Sadly, such is the case for the sublimation data of ionic liquids (or ILs) [1]. ILs are well known for their presumed extremely low volatility [2, 3], and given their prospect use in environmental applications, it is imperative for their properties to be sufficiently explored beforehand, so that potential dangers are eliminated.

In experiment, a pseudo-experimental sublimation enthalpy is obtained by measuring the vaporization enthalpy of the ILs at high temperatures and adjusting the value via the use of isobaric heat capacity and enthalpy of fusion. While transforming a theoretically computed cohesion energy for the purposes of comparison with such measured sublimation properties is a field of study of its own, the fact that it accounts for the largest part of the sublimation enthalpy (at 0 K) means that it is imperative for the cohesion energy to be predicted accurately. The fragment-based additive calculations (FACs) methodology is just one of the tools used to provide results of sufficient quality for this type of problem.

Under the FACs methodology [4], the cohesion energy of ILs is dissected into individual molecular interactions. Short-range interactions are computed on a high level of theory, while long-range interactions are treated with a lower-level method. The methods ought to be chosen carefully, as well as other parameters such as the cut-off distance between regimes and the order of interactions assumed. In the case of ILs, the high-level of theory should be able to sufficiently describe dispersion effects and charge transfer between the ions. Thanks to the presence of long-range Coulomb interactions and many-body effects, the low-level method should also be of sufficient quality for an accurate description. The proper description of all these effects ought to be benchmarked properly, as it is unsatisfactory for FACs-based evaluations to rely e.g. on a fortuitous cancellation of errors, even though it is rather commonplace [5], sadly.

This work focuses on the problems with using DFT-based methods and how the precise choice of basis set and the correction for dispersion and many-body effects affect the results. These effects are benchmarked for three crystalline ILs: [bmPyr][NTf2], [emIm][OTf] and [emIm][pTos]. For the purposes of this benchmark, only two-body interactions are assumed. The results are critically discussed in relation to interaction energies computed with the dispersion corrected MP2C-F12 method.

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# Interaction-induced properties of weakly bound systems in the framework of symmetry-adapted perturbation theory

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Interaction-induced properties are understood as the difference of a given property calculated for the weakly bound complex with respect to the sum of the same property calculated for non-interacting subsystems. Among many quantum chemical methods, symmetry-adapted perturbation theory (SAPT) has been developed for the treatment of such systems. Here we use SAPT to obtain direct expressions for any one-electron property of a dimer. In contrast to the approach proposed by Moszyński, Heijmen and co-workers [1, 2], the presented scheme does not rely on finite-field calculations. We consider calculations of the dipole moment as an exemplary application of the obtained expressions. Numerical results for selected test systems are presented in order to validate the accuracy of the method.

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# Effects of Lateral Interactions on Surface Chemical Reactions Revealed by Kinetic Monte Carlo Simulations with Neural Network Potentials

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## I. Introduction

In heterogeneous catalytic reactions, an atomic-level understanding of the reaction mechanism on the catalyst surface is of great importance. The kinetic Monte Carlo (KMC) simulations have been widely used to link the gap between microscopic aspects derived from first-principles calculations and macroscopic properties. KMC simulates the time evolution of a system based on reaction rates by describing surface states as a set of sites and allows long-time simulations. On the catalyst surface, adsorbed species form a variety of configurations, and lateral interactions among them have non-negligible effects on the adsorption and activation energies. Thus, accurate treatment of lateral interactions is crucial to reproduce macroscopic properties with high fidelity. In this study, we developed a KMC framework that explicitly incorporates lateral interactions, with the aim of clarifying the impact of these interactions on the macroscopic picture of surface chemical reactions.

## II. Method

The time evolution is described based on the rate constant given by

$$k = \frac{k_B T}{h} \frac{f_{TS}^{\ddagger}}{f_{IS}} \exp\left(\frac{-\Delta\varepsilon_0}{k_B T}\right) \tag{1}$$

Here $k_B$ is the Boltzmann constant, $T$ is the system temperature, $f$ is the partition function and $\Delta\varepsilon_0$ is the activation barrier.[1] The rate constants are calculated for all possible elementary processes from the current configuration to determine the process to be executed in the next step. In our framework, $\Delta\varepsilon_0$ is calculated "on-the-fly" for all processes in each step to incorporate lateral interactions explicitly. The neural network potential PFP[2] is used for energy calculations to reduce computational costs. The calculated structures and energies are stored in a database and re-used to speed up the simulations.

## III. Result and Discussion

The present method is applied to hydrogen diffusion on Pd(111) surface (Fig. 1). Compared to the simulation ignoring the lateral interactions, the explicit treatment of the interactions leads to a significant reduction in coverage. The results of CO oxidation reaction on metal surface will be also presented.



**Figure 1:** Time evolution of hydrogen coverage on Pd(111) surface.

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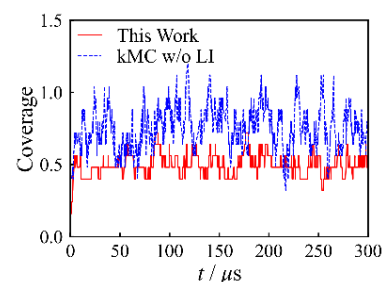[2] S. Takamoto, et al. *Nat Commun* **13**, 2991 (2022).

# The samarium diodide mediated diastereoselective carbon coupling mechanism

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Samarium diiodide is a indispensable reducing agent in organic chemistry because of its unique diastereoselective properties in reductive ring closure reactions.[1] We want to get one step closer to the design of catalytic cycles. Computational investigations of the mechanism lead to better understanding of the reaction order and are necessary for atomistic reaction step insight. We study the ring closure reaction of 5-phenylpentane-2-one[2] at the DFT computational level with PBE0-D3/def2-TZVP//def2-SVP including thermal corrections and implicit solvation by COSMO (THF, $\varepsilon$=7.4). We checked the computational reliability by CAS-PT2 calculations and use an explicitly calculated correction for cosolvent-effects.[3] The proposed reaction path includes single electron transfer (SET), hydrogen atom transfer (HAT) and bond weakening effects when the Sm-complex binds the aromatic site of the precurser. Sterics in the rate determining transition state predict the correct diastereomer of the kinetically controlled reaction. The influence of *para*-substituents clearly rejects a first order concentration dependence on samarium diiodide.

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