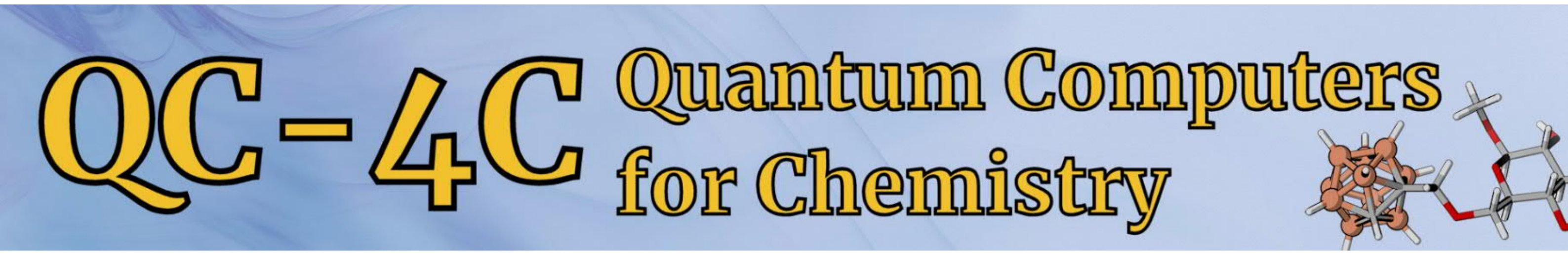
The 36th Winter School in Theoretical Chemistry

QC-4C: Quantum Computers for Chemistry

University of Helsinki, 28 Nov—1 Dec, 2022



Book of Abstracts

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pH-dependent conformational changes in insect odorant binding proteins

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Odorants are hydrophobic molecules that play an important role in insect communication. The transport of these molecules through the aqueous sensillar lymph of insect antennae is mediated by small, soluble proteins called Odorant Binding Proteins (OBPs). The binding mechanism of these odorants to their OBPs is known to be pH-dependent [1]. PBP1, an OBP from Bombyx mori is a well-studied model system, with experimentally determined protein structures in different bound states and at different pH values. These structures suggest that the protein conformation depends on pH, affecting ligand binding affinity. At pH ~4.5 (close to the membrane), the protein exists in a closed form, where the C-terminus forms a helix inside the protein's binding pocket. At neutral pH (in the sensillar lymph), the C-terminus forms a disordered loop, opening the binding pocket for a ligand [2,3].

Based on the experimental structures, possible mechanisms of conformational changes have been proposed [2], but the dynamics of the changes still need to be fully understood. To understand these changes as a function of pH, we studied BmorPBP1 using constant pH molecular dynamics simulations [4,5]. The C-terminus of the protein consists of three acidic residues, suggesting that the conformational changes might occur due to changes in the protonation states of these residues with differing pH. The simulations performed in this study indicate that the C-terminus helix of the protein destabilizes at pH 7 but is stable at pH 4.5. When simulated alone at different pH values, the C-terminus peptide does not show a propensity for alpha helix. However, inside the protein binding pocket, the stability of the helix-protein interaction is pH-dependent, suggesting that the formation of the helix is only possible when it makes stabilizing contacts with the binding pocket. The titration curves obtained from our simulations provide information on the key residues for the conformational changes.

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Description of physicochemical properties and bioactivity of B vitamins by selected methods of computational chemistry

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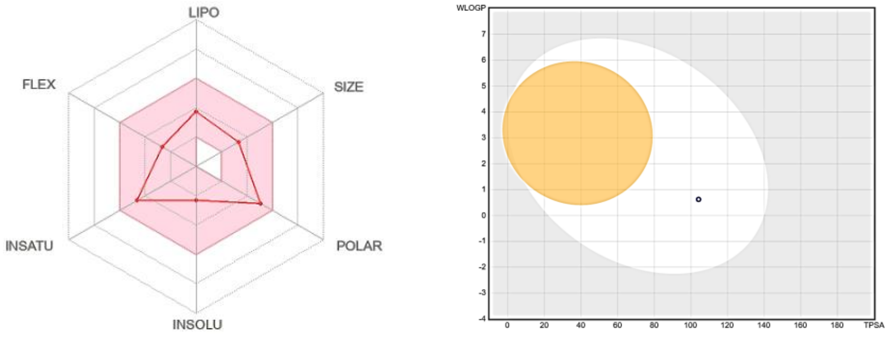
Abstract

This research presents the results of quantum–chemical simulations and *in silico* bioactivity studies of vitamins B.

Quantum-chemical simulations were performed based on **Density Functional Theory** [1,2] at the M06/6–311+G(d,p) and M06/SDD levels of theory [3-5] both in the gas phase and with a solvent reaction field (Polarizable Continuum Model (PCM)) with water as a solvent. The theoretically derived data: the geometrical parameters and spectroscopic signatures of the vitamins B, were compared with the available experimental literature findings (crystal structures and IR spectra).

The description of B vitamins was also enriched by application of cheminformatics tools closely related to the field of Medical Chemistry. It allows us to predict a great number of properties e.g.: logP, logS, TPSA, bioactivity associated with the chosen proteins (like kinases, proteases etc.) or pharmacokinetics (based on compounds' affinity to CYP proteins, capacity gastrointestinal absorption etc.). These studies were done with the use of cheminformatics web tools: **SwissADME** [6] and **Molinspiration** [7]. Their great advantages are wide availability, ease of application, and also solid and quick analysis of small compounds. Thanks to the comparison with literature data of well-known B vitamins, it is possible to confirm that current cheminformatic web tools provide high reliability of the results and can support Drug Design methods.



Results presentations of cheminformatic research carried out by SwissADME:
Bioavailability Radar (left) and BOILED-Egg diagram (right) for thiamine – vitamin B1.

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On the nature of the aurophilic interaction: a quest for covalent and spin-orbit coupling effects

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The term “aurophilicity” describes the tendency of cationic closed-shell gold centres to aggregate in both solid state and solution via intermolecular gold-gold interactions [1]. Despite this effect inducing the formation of a wide variety of supramolecular structures with peculiar properties and possible applications as optically active materials and homogeneous catalysts [2], the nature of the aurophilic interaction remains still poorly understood. This contribution aims to approach computationally the study of the nature of the Au-Au interaction for the simple model [ClAuPH 3] 2 dimer. In detail, several well-established tools for the analysis of chemical bonding (i.e. Energy Decomposition Analysis [3], Natural Orbitals for Chemical Valence [4] and Charge Displacement [5] approaches) will be employed for a thorough analysis of the Au-Au interaction with this dimer. In particular, these studies will focus of understanding, the weight and intimate nature of any covalent contributions to the gold-gold weak bonding. Furthermore, by relying on the use of a 2-component ZORA Hamiltonian, a quantitative assessment of the impact of spin-orbit coupling on the extent of the interaction will be carried out.

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Runtime for Vibrational Structure on Quantum Computers

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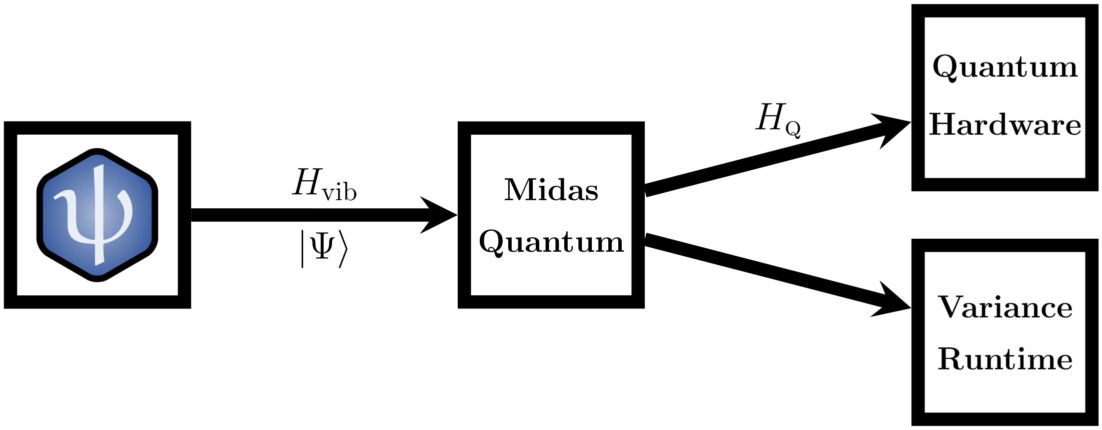
One of the primary challenges prohibiting demonstrations of practical quantum advantages for near-term devices amounts to excessive measurement overheads for estimating relevant physical quantities such as ground state energies. The electronic structure problem on quantum computers has been investigated significantly in recent years while the vibrational structure problem remains relatively unexplored. Importantly, research suggests that classically intractable vibrational structure problems may be solved on quantum computers prior to their electronic equivalents [1].

However, with major differences between electronic and vibrational structure of molecules, the study of resource reductions for estimating anharmonic vibrational states remains relatively unexplored compared to its electronic counterpart. Importantly, bosonic commutation relations, distinguishable Hilbert spaces and vibrational coordinates allow different manipulations of the vibrational system in order to optimize the use of computational resources.

We have thus started the development of a new program package called Midas Quantum that bridges the gap from MidasCpp [2] to quantum hardware. With Midas Quantum we can also estimate quantities of near-term interest, like runtime through variance computations. With MidasCpp and Midas Quantum we can thus explore the dependency of runtime on both the molecular Hamiltonian operator, e.g. vibrational coordinates, and quantum computing preprocessing, e.g. operator grouping schemes.

In this work [3], we investigate the impact of different coordinate systems and measurement schemes on the runtime of estimating anharmonic vibrational states for a variety of three-mode (six-mode) molecules. We demonstrate an average of threefold (twofold), with up to sevenfold (fivefold), runtime reductions by employing appropriate coordinate transformations. Despite such reductions, crude estimates of runtimes for the unitary vibrational CCSD Ansatz and realistic potential energy surfaces are very considerable. Further improvements are thus necessary to demonstrate practical quantum advantages.



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Gold(I)-Containing Light-Emitting Molecules with an Inverted Singlet-Triplet Gap

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Abstract

The so-called INVEST or fifth generation light-emitting molecules feature an inverted singlet-triplet energy gap ($\Delta E_{ST} = E(S_1) - E(T_1) < 0$). [1] A representative example of INVEST molecules is *heptazine* (1,3,4,6,7,9,9*b*-heptaazaphenalene; **Figure 1,** left). [2] Optical excitation leads to a well-defined pattern of charge transfers between neighbouring atomic sites, which is called the multiple resonance (MR) effect (**Figure 1**, right). The origin of the singlet-triplet inversion is still not fully understood, although it is known that contributions from doubly excited configurations increase the required spatial separation of the frontier orbitals. [3]

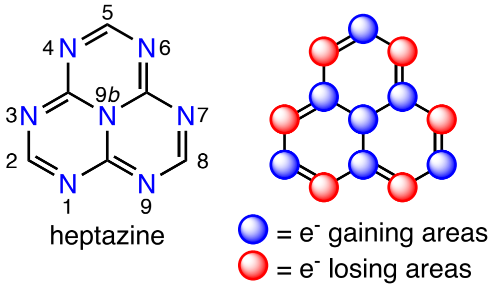

Figure 1. The molecular structure of heptazine (left) and its multiple resonance pattern (right).

As far as we know, no-one has previously taken advantage of the MR effect in gold(I)-containing emitters for obtaining delayed fluorescence from inverted singlet-triplet gaps (DFIST) emission from gold(I) luminophores. Here, we perform the first *in silico* study of gold(I) complexes with an inverted singlet-triplet gap. We propose 2,5,8-tris(dimethylphosphino)heptazine for stabilizing the model compounds. We have constructed three molecules where neutral [Au^IX] (X = Cl (**1**), CN (**2**), C_6F_5 (**3**)) fragments are bound to the lone pair of the phosphorus atoms of the pending dimethylphosphino moieties. Also, direct coordination of cationic $[Au^I(PMe_3)]^+$ fragments to the corners of heptazine has been considered (molecule **4**). We have used DFT and *ab initio* correlated methods (CC2, XMC-QDPT2(12,12)) in calculations of the energy of the lowest excited states and in calculations of the $S_1 \leftarrow T_1$ intersystem crossing (ISC) rate constants (k_{ISC}).

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Searching Stationary Points based on Gaussian Process Regression in Internal Coordinates

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Geometry optimization and transition-state search are two fundamental tasks in theoretical chemistry, i.e. the search for minima and first-order saddle points on the potential energy surface. A reduction of required ab initio calculations leads to a speed-up in computational chemistry. Recently, machine learning becomes popular in computational chemistry. Therefore, Gaussian process regression (GPR) is used to build up a surrogate surface to save computational time and cost.

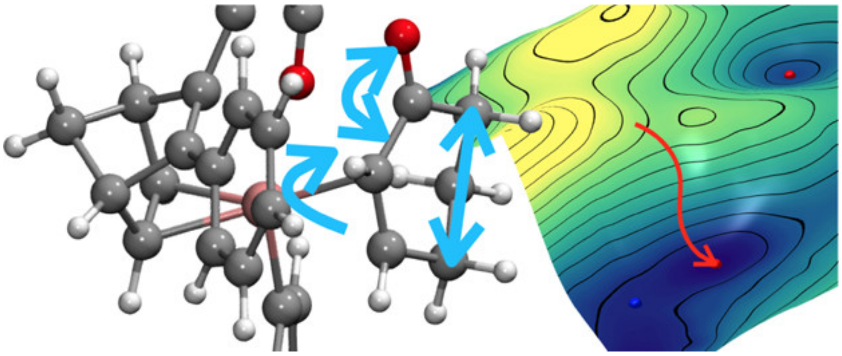

Figure 1: Schematic representation of a geometry optimization [1].

In this work, geometry optimization and transition-state search based on Gaussian process regression are extended to internal coordinates. Delocalized internal coordinates, consisting of bond lengths, bond angles, and dihedrals are used. Two methods for incorporating delocalized internal coordinates are compared for geometry optimization [1]. Both methods train the GPR surrogate surface in internal coordinates. For method one the gradient is predicted in internal coordinates, whereas method two predicts the gradient in Cartesian coordinates. Both methods are tested on 30 small molecules and a large rhodium complex. The first method performs slightly better, while the second method is more robust because it does not depend on an iterative back transformation, which can fail. Both methods reduce the number of required steps compared to GPR in Cartesian coordinates and the standard L-BFGS optimizer.

For transition-state search, only one method is used, because the second method is computationally too expensive for the required Hessian evaluation. To get a good Hessian with only energy and gradient observations, an information-based approach is followed. This so-called acquisition function tries to sample new points, where the most information regards the desired target is expected. If the lowest eigenvalue does not change anymore, regards some threshold, the Hessian is good enough to perform a transition-state search on the GPR surrogate surface.

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Contextuality and memory cost of simulation of Majorana fermions

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Abstract

Contextuality has been reported to be a resource for quantum computation, analogous to non-locality which is a known resource for quantum communication and cryptography. We show that the presence of contextuality places new lower bounds on the memory cost for classically simulating restricted classes of quantum computation. We apply this result to the simulation of a model of quantum computation based on the braiding of Majorana fermions, namely topological quantum computation (TQC) with Ising anyons, finding a saturable lower bound in log-linear in the number of physical modes for the memory cost. The TQC model lies in the intersection between two computational models: the Clifford group and the fermionic linear optics (FLO), a framework analogous to bosonic linear optics. We extend our results and prove that the lower bound in the memory required in an approximate simulation of the FLO model is quadratic in the number of physical modes.

Energy derivatives with a fully differentiable Quantum Phase Estimation algorithm

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Abstract

Quantum computing [1] and differentiable programming [2, 3] are rapidly emerging among the quantum chemistry community as powerful techniques to speed up full-fledged quantum simulations. In order to take genuine advantage of these tools it is mandatory to refine existing algorithms to capture the complexity of chemical systems going well beyond the calculation of molecular energies. Here we report on the extension of a fully quantum differentiable pipeline to compute energy derivatives backpropagating through Quantum Phase Estimation (QPE) circuits. Such an implementation makes geometry optimizations, frequencies and molecular properties' calculations straightforward in a fault-tolerant setting where the QPE algorithm is one of the most promising alternatives. Building on the work of Cruz *et al.* [4] we provide a statistical analysis on a smooth energy estimator that allows differentiability of the quantum subroutine. We tested our implementation on the H_3^+ molecule performing both ground and excited state geometry optimization and estimate the dipole moment at different geometries computing derivatives w.r.t. an external electromagnetic field. Finally, we compare this approach to other existing methodologies developed to compute energy derivatives.

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O–O BOND FORMATION AT Co(IV)–OXO CENTER

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Electronic structure calculations of a cobalt-based catalyst, $Co_3(BO_3)_2$ were performed utilizing the multi-configurational Complete Active Space Self Consistent Field (CASSCF) method. Our calculations show that the ground states were overall quartet spin states and the low spin (LS) doublet and high spin sextet (HS) were well separated. Therefore, the reactivity is due to the intermediate spin state. The HS states experiencing more amount of exchange are lying lower than the LS states. The boron environment yields a more elongated Co–O bond (1.638 vs 1.625 Å) compared to an all-oxygen ligand coordination. The O–O bond forming species has a mixed Co–oxo/oxyl character and nucleophilic attack of water to the cobalt-oxo intermediate is critical for product formation. Co–O bond is weaker and the LUMO is more electrophilic in the cobalt-borate intermediate, which makes it a more reactive species towards the nucleophilic attack of water. Electrophilicity of the Co–oxo/oxyl center can be probed by molecular orbital analysis and might be a useful tool for realization of new Co species for WOC.[1-3]

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ADC(4): The fourth-order algebraic diagrammatic construction scheme for the polarization propagator

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Abstract

Until today, perturbation-theoretical consistent algebraic diagrammatic construction (ADC) schemes for the polarization propagator had been derived and implemented up to third order [1]. They have turned out to be versatile and reliable ab initio single-reference methods for the quantum chemical investigation of electronic transitions as well as excited-state properties. Here, we present, for the first time, the derivation of consistent fourth-order ADC(4) schemes exploiting novel techniques of automated equation and code generation [2]. The accuracies of the resulting ADC(4) excitation energies have been benchmarked against recent high-level, near exact reference data [3]. The mean absolute error for singly and doubly excited states turns out to be smaller than 0.1 and 0.5 eV, respectively. These developments open also new avenues toward highly accurate ADC methods for electron-detached and -attached states.

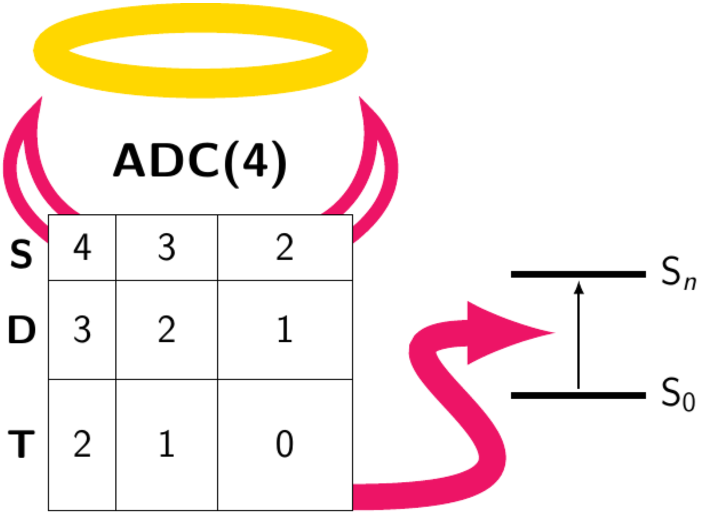

Figure 1. ADC(4) matrix.

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CSC services for computational science

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CSC – IT Center for Science Ltd. is a Finnish centre of expertise in ICT that provides world-class services for research, education, culture, public administration, and enterprises, to help them thrive and benefit society at large. CSC provides computational and data storage solutions to enable our customers to perform research to the best of their abilities without worrying about access to the best tools of their trade.

Presently, two national supercomputers are available to researchers affiliated with a Finnish research institution: Puhti and Mahti. CSC also hosts the pan-European supercomputer LUMI, which is available to academic and industrial users across Europe. LUMI is the most powerful supercomputer in Europe, and number three in the world according to the TOP500 project [1]. The supercomputers provide both CPU and GPU nodes, some with fast local disks.

The reproducibility of scientific findings is a major issue of academic research. Open data available in a public database is key to ensuring that others can take the same raw data and reproduce or extend published work. For this, long-term data storage is needed. Researchers can use the Allas storage service for that purpose. CSC also provides resources for handling sensitive data, running virtual machine instances for cloud computing, and more.

CSC, VTT, and Aalto University maintain and develop the Finnish Quantum-Computing Infrastructure FiQCI [2]. From November 2022, pilot access to Finland's first quantum computer, Helmi, co-developed by VTT and IQM Quantum Computers is available, marking the onset of the age of quantum-accelerated supercomputing. In the near-future, access to several additional quantum computers will open up for European users through the LUMI-Q consortium [3].

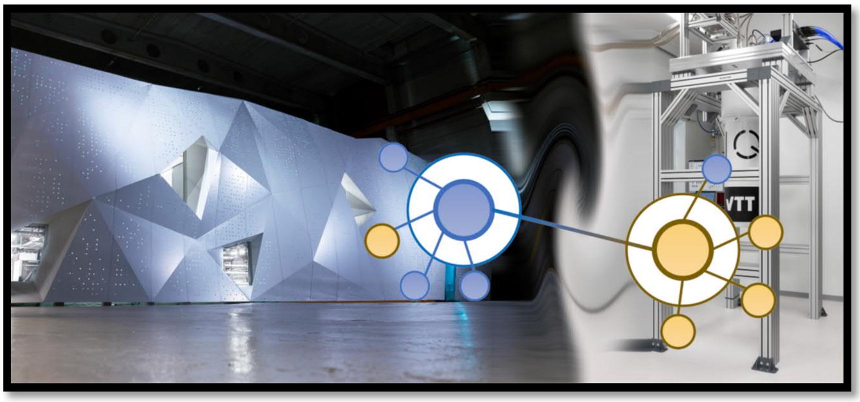

Figure. The LUMI supercomputer is now connected with the Helmi quantum computer.

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Computational study of efficient perovskite solar cells employing simple carbazole as hole transporting materials

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Abstract

Perovskite solar cells (PSCs) have attracted worldwide attention due to their improved power conversion efficiency (PCE) and ease of fabrication processes[1-2]. Hole transport materials (HTMs), an important active material in PSCs, are responsible for efficiently extracting holes at the perovskite/HTM interface and preventing unwanted charge transfer processes, thereby enhancing device performance. In this study, we focus on different carbazole-based HTMs and investigate the effect of π bridge on their structural and optoelectronic properties. The calculations are based on density functional theory, time-dependent density functional theory and Marcus theory. Important parameters such as electronegativity, solubility and stability, absorption and emission spectra, stock shift, exciton binding energies, and frontier molecular orbitals are identified and discussed.

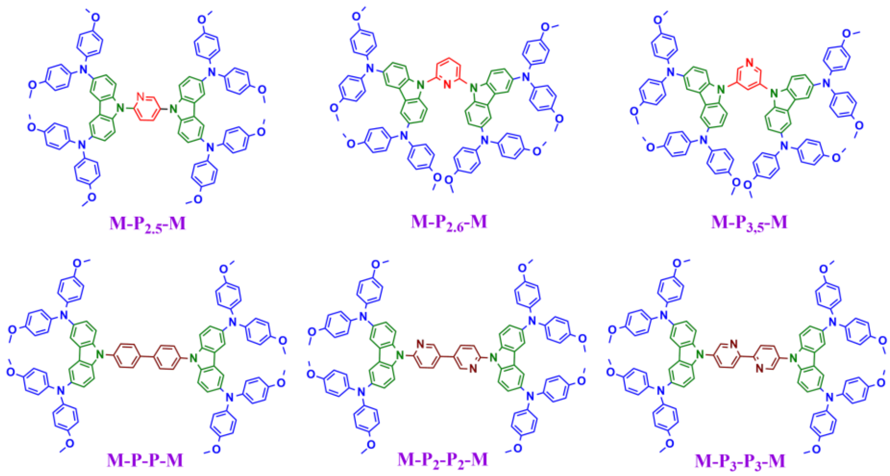

Figure 1: Molecular structures of some of our investigated HTMs.

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Simulating dephasing-assisted quantum transport with digital quantum computers

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Simulating charge and energy transfer in extended molecular networks requires an effective model to include the environment because it significantly affects the quantum dynamics. A prototypical effect, known as environment-assisted quantum transport (ENAQT), consists in the enhancement of the transfer efficiency by the interaction with an environment [1]. A simple description of this phenomenon is obtained by a quantum walk over a molecular network in the presence of inter-site decoherence. We have considered the simulation of the dynamics underlying ENAQT with a digital quantum computer [2]. The problem is non-trivial as it requires an representation of the reduced system non-unitary dynamics in terms of quantum gates. We have adopted two different algorithmic approaches: the first one based on stochastic Hamiltonians [3,4] and the second one based on collision models [5,6]. We have tested both algorithms by simulating ENAQT in a small molecular network on a quantum computer simulator (namely Qiskit QASM) and provided a comparative analysis of the two approaches. Both algorithms can be implemented in a memory efficient encoding with the number of required qubits scaling logarithmically with the size N of the simulated system while the number of gates increases at worst with $\mathcal{O}\left(N^3\right)$. We found that the algorithmic quantum trajectories generated by the two simulation strategies realize distinct *unravellings* of the open system dynamics.

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Variation of the counterion and the ligand coordination in chiral Rh-diene complexes for an asymmetric 1,2-addition

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Abstract

This work is based on experimental studies, in which for each counterion, the reaction was carried out under homogeneous conditions using dioxane as a solvent and also in a microemulsion to investigate the influence of the confinement on the catalytic activity and enantioselectivity. In the experimental results, when applying the acetate as counterion the yield increases from 9% in dioxane to 52% NMR yield when using the microemulsion. For the other anions, the microemulsion also slightly increases yields and enantiomeric excesses. These experimental results can be rationalized by the calculations because the binding energy of the acetate is much higher than for the other anions and therefore the activation of the catalyst through the anion exchange of the acetate by a hydroxide anion is less favoured. The use of the microemulsion might facilitate the activation process and therefore lead to higher yields.

Furthermore, different coordination possibilities of the ligand to the Rh were investigated for eleven ligands with different spacers. Coordination of the triazole unit to the Rh is favoured by around 100 kJmol^{-1} compared to the elongated spacer except for one ligand where the coordination of the oxygen from the spacer is favoured also by around 100 kJmol^{-1} compared to the elongated spacer.

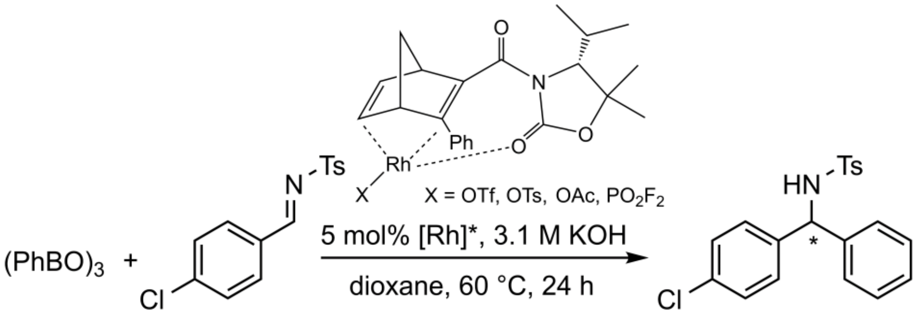

Figure 1. Reaction equation of the Rh-catalyzed asymmetric 1,2-phenyl-addition of triphenylboroxine to N-tosylimine and schematic representation of the Rh-complex with the different counterions.

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The Reaction Fragility Spectrum in solvent obtained with C-PCM model

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Abstract

Recently we have introduced and developed the Reaction Fragility Spectrum (J. Chem. Phys. 2017, 147, 134109, J. Phys. Chem. A, 2020, 124 (6), 1076-1086) as a convenient and instructive method of visualization of electronic reorganization in a reacting molecular system. This method relies on tracing the evolution a divergence of the Hellmann-Feynman forces and to represent elasticity of the atomic structure over the reaction progress. Depiction of the course of the reaction is achieved by a diagram, analogous to a spectrum, that correlates with the formation and breaking of bonds. This work provides analysis and the numerical results of the effect of the solvent influence on the mechanism of the reaction revealed by the Reaction Fragility Spectrum [Fig. 1]. Our results show how the sites positions on the IRC path of bond breaking and forming depend on the solvent and its dielectric constant.

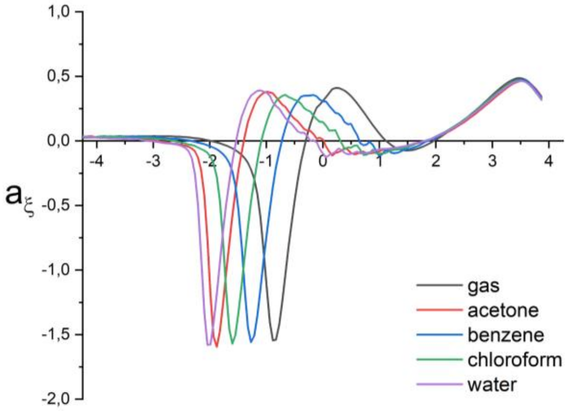

Figure 1. Summary reaction HF + CO → HCOF fragility for solvents

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Calculations have been carried out in Wroclaw Centre for Networking and Supercomputing (https://www.wcss.pl), grant No. 249

Understanding Battery Materials: An Insight into Different Systems via DFT

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The focus of this work is on the calculation of different material properties and reactions in battery systems with emphasis on the room temperature (RT) Na-S system, by using Density Functional Theory (DFT). Since RT Na-S batteries raise, despite their excellent theoretical electrochemical properties, a number of different issues, theoretical calculations, with their ability to provide atomistic insight are of great importance in exploring new battery materials for the future.

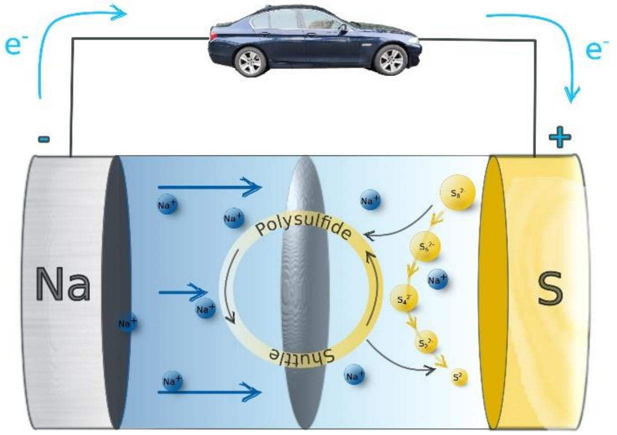

Figure: Schematic representation of the functional principle of a RT Na-S battery.

One application is the investigation of the high conductivity of a new conducting salt Na-PPB (sodium bis(perfluoropinacol)borate) as part of the electrolyte in a RT Na-S system [1]. Compared to a standard conducting salt, it can be shown by nudged elastic band (NEB) calculations that Na-PPB causes a higher Na^+ mobility, which explains the better electrochemical performance.

In a different application we investigate the influences of an in situ crosslinked Gel Polymer Electrolyte (GPE) in a RT Na-S system on the ionic mobility in comparison to liquid electrolyte [2]. Through the calculation of the Molecular Electrostatic Potential (MEP) map of the GPE monomer, various binding sites are visible. Binding energies of the fully solvated Na^+ compared to the GPE coordinated Na^+ are showing higher absolute values which forces ion hopping in the GPE and thus a high ion mobility despite the high GPE viscosity.

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H-Bond Framework 1.0
Comprehensive empirical model of substitution

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Abstract

Rational resource management, viability and CPU-to-laboratory transitionability are one of the fundamental aspects of modern drug and materials design. The first step to smart design and assessment of compounds was proposed. A unified description of the substituent effect on the intramolecular hydrogen bridge was developed on the basis of over 500 tri-ring aromatic Schiff bases [1] with different substitution patterns. Both proximal and distal effects were investigated using Density Functional Theory (DFT) [2,3] in the gas phase and with Polarizable Continuum Model (PCM). [4] In order to characterize the non-covalent interactions, a topological analysis was performed using Non-Covalent Interactions (NCI) index. [5] The generalized composite substituent effect was divided into the increments describing the different interactions of the hydrogen bridge and the substituent: the classical substituent effect, involving resonance and induction mediated through the ring and steric effect based on substituent proximity to the bridge elements.

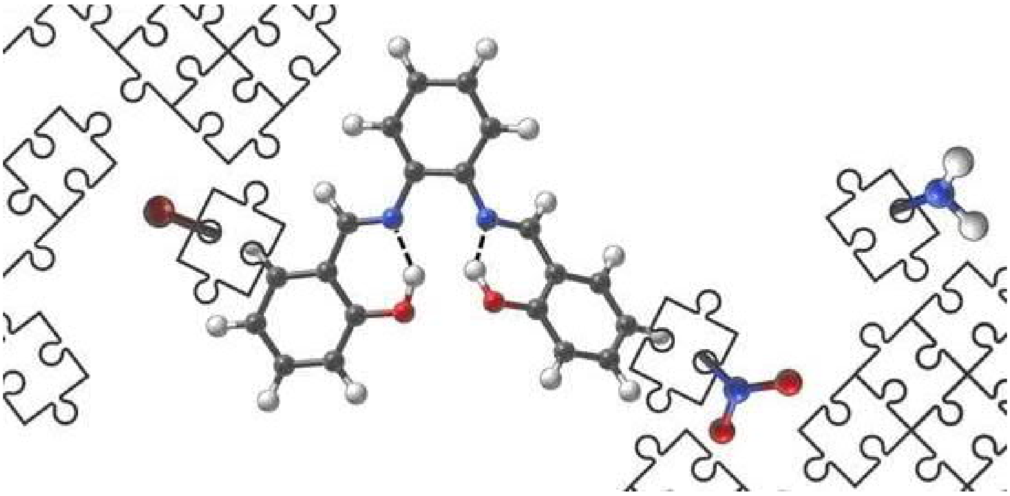

Figure 1. Graphical abstract.

Acknowledgments

The Authors thank Wrocław Centre for Networking and Supercomputing (WCSS) and Poznań Supercomputing and Networking Center (PSNC) for generous CPU time resources and use of file storage facilities.

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Sampling from water molecules conformations arranged in a lattice space with quantum computer

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Abstract

Molecular dynamics and Monte Carlo methods have proved to be effective tools for studying molecular systems at zero temperature (and thus finding the minimum energy configuration) or at finite temperature for sampling from a statistical set. These methods over the years have been widely used compared to combinatorial methods due to the high computational cost involved in the latter.
With quantum computers, people have begun to think that studying a molecular system combinatorially may be more advantageous instead [1]. To date, quantum devices are not yet able to handle long calculations due to high noise but there are algorithms such as the Variational Quantum Eigensolver (VQE) and the Quantum Approximate Optimization Algorithm (QAOA) that allow to address combinatorial optimization problems through the joint use of classical and quantum processors. In this paper we will use variations of these two quantum optimization algorithms [2] to compute the ground state of a lattice of water molecules interacting with each other through the formation and destruction of hydrogen bonds. The system is then completed with the addition of an ion that interacts with the electric dipoles of the water molecules.
To achieve the minimum energy of these systems via the VQE and QAOA algorithms we have rewritten the water lattice Hamiltonian into an Ising Hamiltonian since from an Ising system it is easy to write a diagonal Hamiltonian operator with respect to the computational basis of the qubits of the device.

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QM/MM Simulations of Biological Systems using Novel GROMACS- CP2K Interface

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Simulations of chemical reactions pathways can provide an atomistic insight into many biological and chemical processes. To perform such kind of modelling in complex systems, that includes solvent and/or proteins Multi-scale Quantum Mechanics / Molecular Mechanics (QM/MM) approaches are often used. Here we introduce a whole new interface to perform QM/MM simulations in fully periodic systems using MDModules that couples GROMACS with CP2K quantum chemistry package. This enables hybrid simulations of systems in systems where chemical reactions occurs. The interface supports most of the simulations techniques available in GROMACS including: energy minimization, classical MD and enhanced sampling methods such as umbrella sampling (US) and accelerated weight histogram (AWH) to perform scalable modelling of reactions inside biological systems.

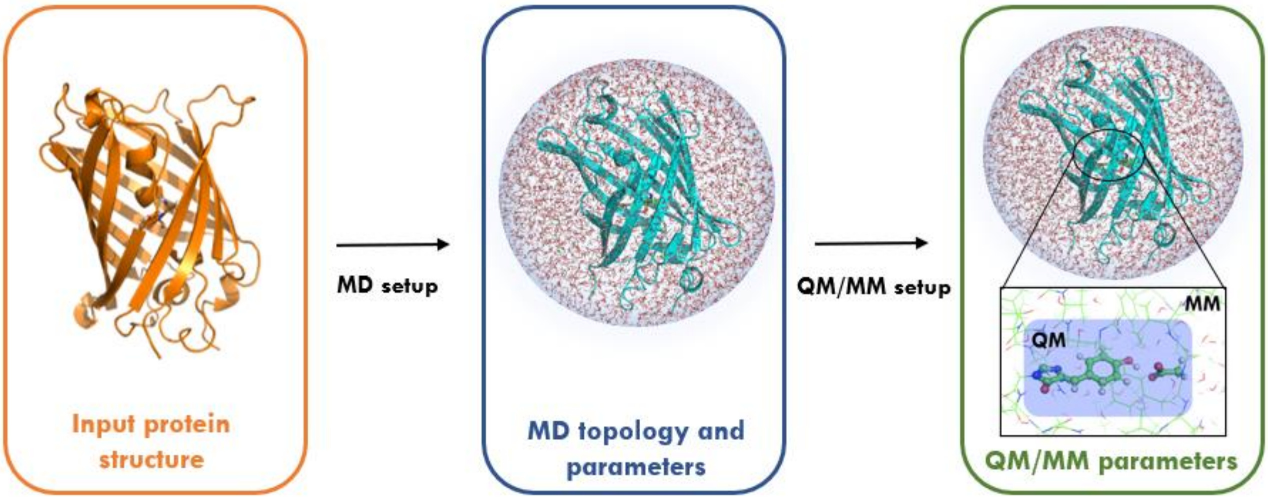

Figure 1. Workflow of QM/MM simulations with GROMACS-CP2K interface.

On the magnetic response to quantify aromaticity: The role of orbital contributions

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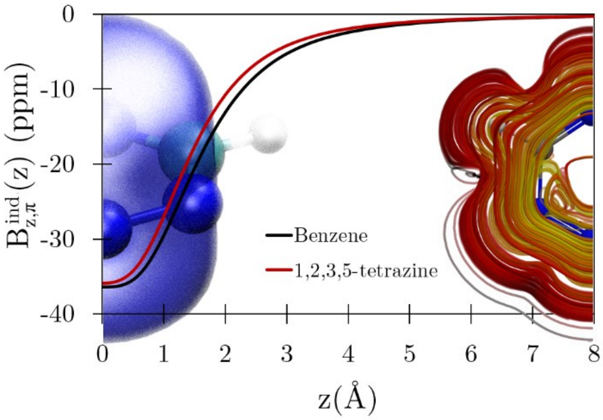
At present, quantification of aromaticity in terms of the molecular magnetic response is commonly performed by calculating some quantity related to the induced current density or the induced magnetic field.[1,2] In particular, the analysis of current densities allows visualization of current pathways, showing the existence of ring currents, as the numerical value of the current (called the ring-current strength). On the other hand, the induced magnetic field allows visualize the direction of the field to determine the shielding and deshielding regions. The size and shape of the so-called shielding cones allow estimation of the degree of aromaticity. Not only that, both techniques allow dissection into orbital contributions of these fields. This makes it possible to determine which block of orbitals contributes to aromaticity, which is helpful for systems with multiple aromaticity.

In this work, we analyze the interaction of molecules within Ramsey's theory to diagnose the degree of electron delocalization considering the corresponding warnings when using magnetic criteria. The role of the molecular geometry, topology, curvature, and the orbital contributions to the magnetic response are investigated within the framework of density functional theory (DFT).[3-6] The analysis focuses on the computation and visualization of induced magnetic fields and the magnetically induced current densities and their relationship to each other.



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A new quantum graph community detection method for reducing the complexity of the molecular structure computation

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Abstract

Following the main ideas from [1], which suggest using a quantum community detection method for finding approximate diagonal blocks in molecular Hamiltonian matrices related to the Full Configuration Interaction (FCI) theory. Their community detection method is a quantum version of a standard classical method, which uses so called modularity maximization. It is formulated as a quadratic unconstrained binary optimization problem (QUBO), which can be solved on quantum annealers like D-Wave machines. The method seems to be effective in many sample cases. However, for a $n \times n$ matrix with number of communities $= k$, the method uses $k \times n$ qubits. Further, one needs an extra term in the QUBO to ensure that every node belongs exactly to one community.

In this work, we suggest a new quantum community detection method which is in our opinion more 'quantum friendly'. It is a further development of our 'community panning' method [2]. Instead of modularity maximization, we take graph-theoretic concept of 'regularity', which is a key concept in so called Szemerédi´s regularity lemma. We used Tao's formulation [3] of the regularity, which is well suited for quantum implementation. We end up with a energy function $L(S) \coloneqq \sum_{ij}(s_i s_j (d - w_{ij}) + s_i (1 - s_j)(w_{ij} - d))$, in which $S = (s_1, \dots, s_n)$ are binary variables, d is average weight of the weight matrix W. The first term indicates high weight inside a community while the second one low weight of a community to the rest of the graph. The method starts from a weight matrix created from the Hamiltonian matrix with the rule: $w_{ij} = |H_{ij}|\delta_{ij}$, in which $\delta_{ij} = 1$, if $i \neq j$ and 0 otherwise. The first community corresponds to the configuration S which minimizes L, the submatrix of W corresponding to this solution is deleted and the process is repeated on the remaining submatrix and so on until all communities are found. The algorithm was tested on D-Wave quantum annealer with promising results, comparable of those in [1]. A quantum gate version using the Quantum Approximate Optimization Algorithm (QAOA) is also available and tested in a smaller scale.

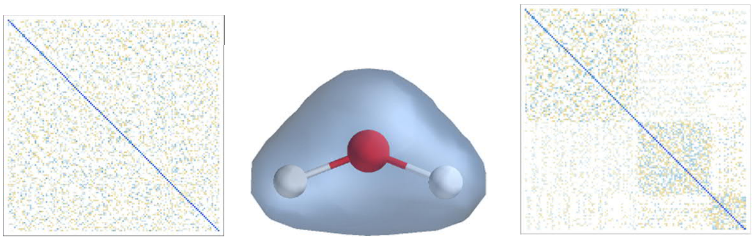

Figure 1. Testing a new community detection method for finding approximate block diagonal structure (right) of the Hamiltonian matrix (left) of the water molecule (middle)

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Estimation of the partition function of an ice crystal exploiting thermal noise in quantum annealers

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Abstract

Estimating the partition function of a molecular system is both a relevant and difficult problem. Such estimation allows the calculation of many useful thermodynamical quantities, but it requires to estimate complex integrals. This is usually done by generating a lot of thermally distributed configurations of the system via Montecarlo methods. Using such methods, it is often difficult or extremely expensive to approximate partition functions of systems where thousands of molecules are involved.

Adiabatic quantum computing (AQC) is a promising new approach to tackle the partition function estimation problem. AQC devices are built to solve quadratic binary optimization problems, but their internal noise is mainly thermal, which makes the device a great Boltzmann distribution sampler [1]. Thus, AQCs can be used to produce the samples needed to estimate the partition function of any system whose energy function can be mapped to the energy functional of a quantum Ising system. This is a novel application for quantum annealers.

We consider a hexagonal ice crystal, and we show how to map its energy functional to an Ising system with minor approximations, using the correct geometry and position of the molecules. Such implementation is optimized to reduce the number of binary variables used in the corresponding Ising system.
Then, the D-Wave Advantage AQC device is used to sample from such Ising system to estimate the partition function of an Ice crystal.

Further studies to be conducted: study hydration of an Ion introduced in the water lattice.

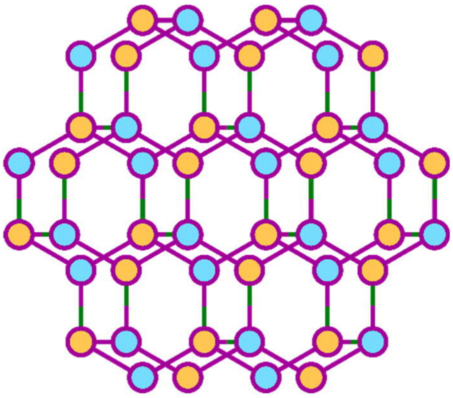

Figure 1: Topological structure of hexagonal ice (Two layers). To optimize the number of qubits used, green edges are represented in the cost function using an appropriate combination of the other edges.

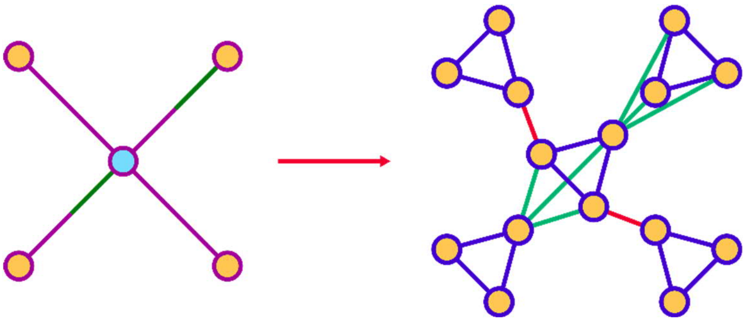

Figure 2: topological mapping of the crystal graph of a single molecule on the Ising system that is then mapped onto the physical quantum annealing device.

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Hyperparameter Optimization of Quantum Annealing Boosted Restricted Boltzmann Machines

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Abstract

A novel variation of quantum computing called quantum annealing has shown promise in tasks, which require sampling from probability distribution called the Boltzmann distribution. This probability distribution is featured quite often in various machine learning tasks, of which the training process of Restricted Boltzmann Machines is probably the most featured occurance. This machine learning model is quite common in the pretraining process of some deep learning models like in deep belief networks. Quantum annealing has been shown to be an effective tool for estimating this probability distribution, sometimes even outperforming classical approaches. As the amount of qubits in these devices increase over time, the applicability of these techniques approach quickly the realm of practicality.

One key issue around using this technique in practice is that applying quantum annealing introduces multiple new hyperparameters for the sampling tasks, making the process of choosing parameters quite convoluted. Even worse, the most optimal parameters seem to change depending on the system that is being estimated, meaning that the best initial choice of parameters might not be suitable for the final steps of the training algorithm.

Our contributions for this challenge is the development and testing of various hyperparameter optimization algorithms, which aim to find some sense to what sort of parameter optimization methods are the most suitable for using quantum annealing in the process of training Restricted Boltzmann Machines. We use common metaheuristics like Grid Search and Gaussian Processes to seek out these parameters, while also testing more advanced methods for determining whether more granulated choice of the device parameters is a good idea during training. Lastly we evaluate the performance of these methods in two dimensions: model performance and how much computational time these algorithms require from the quantum annealing device.

Automatic derivation of expressions of Symmetry Adapted Perturbation Theory

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Abstract

In many phenomena relevant to the physical, chemical and biological sciences, relatively weak intermolecular interactions play a key role. The study of these interactions is possible, among other things, by theoretical methods of calculating the intermolecular interaction energy. One of these methods is the Symmetry Adapted Perturbation Theory (SAPT) [1, 2].

The derivation of expressions that can be implemented numerically for theoretical methods based on Symmetry Adapted Perturbation Theory requires many operations on very long sequences of symbols, additionally containing many indices. Therefore, automation of this process allows one to simplify the task and eliminates a potential source of errors.

Authors developed a computer program based on the second quantization approach and Wick's theorem, which enables one to generate expressions describing corrections to the intermolecular interaction energy for methods based on Symmetry Adapted Perturbation Theory. The developed code takes the form of a module for the Python programming language. It is based on the SymPy [3] library for symbolic calculations.

The developed code was successfully used not only for reproducing well known formulas, but also for generating new expression describing the correction to the first-order exchange energy in an approximation accounting for the exchange of up to two electron pairs between interacting monomers described at the Hartree-Fock level.

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Quantum Circuit Learning Method for Predicting SQL Query Metrics

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Structured Query Language (SQL) is the most used relational database query language in the world. In modern applications, data volume, variety, and connectivity have increased. Querying data should not become a bottleneck in data-intensive applications.

Query processors in relational databases can assign SQL queries to various measurements, such as cardinality, cost, and execution time estimations [1]. The optimization of the query heavily depends on the estimates. Usually, the problem is solved with machine learning, dynamic programming, or integer programming.

As far as we know, our work is the first attempt to apply quantum computing and quantum circuit learning as a part of the SQL query optimization pipeline. Even if we cannot beat the classical methods with the current quantum hardware, we can point out its limitations, understand quantum computing frameworks in a circuit learning context, and propose novel methods to model the problems with quantum computing algorithms. Especially quantum computing and machine learning are a promising combination because both are based on linear algebra and probability theory. Quantum computing also provides a lot of useful terminology which can make quantum machine learning algorithms explainable.

We utilize methods from quantum natural language processing (QNLP) [2] and quantum circuit learning [3]. First, we parse SQL queries and represent them using context-free grammar (CFG) diagrams. The CFG diagrams are functorially mapped to pregroup grammar diagrams. We perform a rewriting process for the pregroup grammar diagrams to optimize and reduce their size. We functorially translated them into parameterized quantum circuits. We optimize the circuit parameters using simultaneous perturbation stochastic approximation algorithm.

This is still ongoing work, and many demonstrations can be found on Github [4]. Currently, we are at the phase where we can represent SELECT-FROM-WHERE type of SQL queries with complex filtering and join expressions using pregroup grammar diagrams and parametrized circuits. The results from QNLP [5] are promising and our results are in line with the previous research. We are excited to be able to express SQL queries as parametrized circuits and utilize the quantum circuit learning methods.

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Machine learning for interatomic potential models

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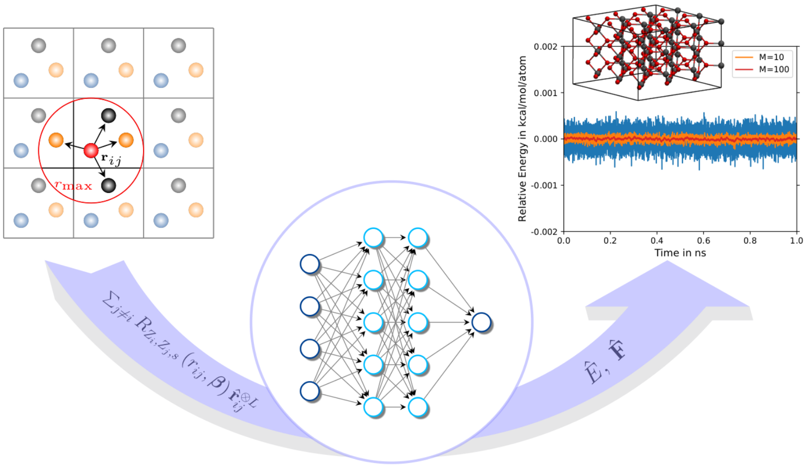
Abstract

Machine-learned interatomic potentials are gaining importance in computational chemistry due to their computational efficiency comparable to empirical force fields and accuracy on par with the reference *ab-initio* methods. Here, the methodology developed in the lab of Prof. Kästner for constructing computationally efficient and accurate interatomic potentials, referred to as Gaussian moment neural network (GM-NN), is presented [1, 2].

The GM-NN approach uses neural networks (NNs) to map novel symmetry-preserving local atomic descriptors, Gaussian moments (GMs), to auxiliary atomic quantities and includes both the geometric and alchemical information about the atomic species of both the central and neighbor atoms. The construction of GM features is based on defining pairwise distances between neighboring atoms, splitting them into their radial and angular components, and constructing Cartesian tensors from them. Thus, the key idea of the GM representation is to apply equivariant transformations to the inputs, i.e., spatial coordinates, prior to computing rotationally invariant scalars. Besides the conventional property prediction, we introduce the uncertainty estimate for NN-based machine-learned potentials employing gradient features corresponding to the finite-width neural tangent kernel [3, 4]. Moreover, we demonstrate how to enforce the diversity and representativeness of the selected structures.

Finally, we demonstrate the broad applicability of the presented approaches ranging from the conventional modeling of high-dimensional potential energy surfaces to the description of spin-phonon relaxation processes [5, 6].



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QM/MM MD simulations of horizontal proton transfer pathways in the antiporter-like subunits of mitochondrial respiratory complex I

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Abstract

The molecular mechanism of respiratory complex I (NADH:ubiquinone oxidoreductase) has remained one of the biggest mysteries in bioenergetics. Being the largest enzyme in the respiratory chain, it couples the electron transfer process to proton pumping across the inner mitochondrial membrane, spatially separated by ~200 A from one another. This phenomenon raises an enigmatic question: how does the energy released from the redox reaction can be transmitted for such long distances? In our work, we advocate the hypothesis that it can be accomplished by the translocation of protons along the central hydrophilic axis of the enzyme - a highly hydrated region revealed by the structural data [1-4]. We utilise state-of-the-art quantum mechanical/molecular mechanical (QM/MM) simulations to study the dynamics of horizontal proton pathways in the high-resolution structure of respiratory complex I from *Yarrowia lipolytica* [4]. We apply QM/MM free energy umbrella sampling simulations to various proton routes bridging highly-conserved protein residues of the ND2 subunit of the enzyme. Our results show low free energy barriers and favourable thermodynamics for the proton pathway laterally spanning the entire ND2 subunit. For the first time, we emphasize the critical role of tyrosine residues in coordinating the transmission, and show reasonable energetics for the proton transfer in interfacial regions of the ND2 subunit with the adjacent ND4L and ND4 subunits. Our results elucidate the long-range energy translocation processes in the membrane part of the enzyme, casting doubts on the canonically admitted proton pumping models in respiratory complex I.

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