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Posters Sessions

Schrödinger, Born and Kohn: Pioneers in Theoretical Chemical Physics

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This talk will describe the careers and contributions to theoretical chemical physics of Erwin Schrödinger, Max Born, Walter Kohn and their associates. The presentation will be based on original research carried out by the speaker for three recent books [1-3].

[1] D. C. Clary, *Schrödinger in Oxford* (World Scientific, March 2022).

[2] D. C. Clary, *The Lost Scientists of World War II* (World Scientific, March 2024)

[3] D. C. Clary, *Walter Kohn: From Kindertransport and Internment to DFT and the Nobel Prize* (World Scientific, November 2024).

Theoretical chemistry based on the exact solutions of the scaled Schrödinger equation

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In natural science, the so-called "God Equation" is important. Newton's equation of motion is an example. It is solvable and its exact solutions on astronomy were useful for preparing calendar and space rockets. On the other hand, for chemical worlds, quantum mechanics is the principle and the exact solutions of the Schrödinger equation (SE) are crucial. However, unfortunately, this equation was considered "insolvable", for long, except for the hydrogen atom. Therefore, the benefits like those Newton's low produced, could not be expected in the chemical world.

In 2004, however, the theory for solving the SE was discovered [1]. A reason of its insolvability lied in the incompleteness of the SE itself: its variational formula diverges to infinity, instead of zero as the variational principle demands. Then, the author proposed the scaled Schrödinger equation (SSE), $g(H - E)\Psi=0$, where g is the scaling function, positive always. The SSE is equivalent to the SE, but its variational formula does not diverge. Therefore, the SSE is the correct basic equation of the quantum mechanics. Further, the author derived the general theory for solving the SSE, called Free Complement (FC) theory. Thus, the same road as for the Newton's low had been opened.

When the SSE and the FC theory were applied to Li_2 molecule, the calculated potential curves of the lower 9 valence states completely overlapped with the elaborate experimental curves [2]. Thus, the SSE, equivalent to SE, became solvable with the FC theory. Thus, a fruitful way has been opened in the field of quantum mechanics. We are currently developing this road and the topic today is its progress report.

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MP2 made better and faster?
Recent developments in regularization and local correlation

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Rayleigh-Schrodinger perturbation theory, and its ab initio application to many-electron systems via Moller-Plesset (MP) perturbation theory, are not regular order by order, and therefore can exhibit erratic behavior for systems with small HOMO-LUMO gaps. In the first part of this talk, I will discuss a new approach to regularize MP2 theory against divergence in the small gap limit, based on modifying Brillouin-Wigner perturbation theory to be size-consistent as well as regular at second order. The extent to which these advanced regularizers need to be system-specific versus universal will be discussed.

My second topic is revisiting the design of local correlation methods at the MP2 level, for its own sake, and well as a prototype for higher order methods. In our view, the main challenge for local correlation is to achieve full control over errors such that a user only needs to select a single numerical drop tolerance. To achieve this goal, we have designed a new “single threshold” approach to local MP2, that also avoids use of projected AOs and PNOs to span the virtual space, by instead employing a localized orthogonal virtual basis. Accuracy and performance will be assessed via a range of example calculations.

Nucleophilic Addition : Input from computations from the Felkin-Anh rule to the Grignard reaction

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The study of the Grignard reaction is part of our long-standing interest in the study of nucleophilic addition [1]. Many years ago, calculations could be performed using very simplified models of the reagents. These very simplified models of the chemical systems were successful in providing qualitative insights for many reactions [2]. Today, it is possible to model reactions using realistic representations of the chemical species and methods that represent properly the thermodynamics of complex systems. We have looked at the Grignard reaction in an attempt to provide insight into a reaction, which has remained elusive despite extensive studies since its discovery in 1900. We will present the arguments that led us to believe that the Grignard reaction occur via numerous parallel pathways[3,4]. We pursue with the study of lithium salts (LiX, X = halide) (5) with the goal to understand the role of additives such as LiCl[6] in the reaction.

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ΔSCF Excited-State Approach: Theoretical Foundation, Linear Conditions for Fractional Charges, and Physical Meaning of Orbital Energies

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Since the 1970s, the Kohn-Sham functionals, while formulated only for ground states, have been employed for ΔSCF calculations of excited states, achieving accuracy comparable to ground state results, despite a lack of theoretical justification. Furthermore, our recent functional development overcoming the systematic delocalization error associated with commonly used approximations leads to orbital energies accurately approximating the corresponding quasiparticle energies, which are the ionization energies and electron affinities to ground and excited state electron removal and addition states. Both observations indicate that the functional theoretically formulated and approximations constructed for grounds states contain excited state information.

Indeed so. We establish the theoretical foundation for ΔSCF calculations of excited states, showing that it is necessary to go beyond electron density and use the first-order density matrix of the noninteracting reference system to define the energy functional. While the minimum of the same functional corresponds to the ground state energy, consistent with ground state DFT, the stationary solutions yield excited-state energies and electron densities, establishing the foundation of ΔSCF calculations.

We extend the theory to fractional charges and show that the exact energy functional for fractional charges, expressed as a linear combination of the density matrix of an N −electron and that of an (N + 1) −electron excited state, is a straight line interpolating the energies at integers. We introduce the concepts of excited-state chemical potentials to describe the slopes of these linear lines. Numerical calculations reveal the excited-state delocalization error with common approximate functionals but good performance of corrected functionals on the proven linear conditions. Finally, we prove the general chemical potential theorem: the noninteracting one-electron orbital energies in DFT ground states and ΔSCF excited states are corresponding chemical potentials of electron addition or removal, from an N -particle ground or excited state to an (N ± 1)-particle ground or excited state.

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Quantum chemistry of core-level states

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Spectroscopy is a powerful tool for interrogating the matter. Techniques exploiting X-ray offer unique insights. However, decoding the message delivered by the spectra is far from trivial. How do we convert the spectra into what the nuclei and electrons are doing? The theoretical modeling provides a way to do so. This lecture will discuss new and old challenges faced by quantum chemistry in the context of modeling electronic structure in high-energy regime and highlight recent progress in many-body methodology in treating spectroscopic signatures of core-vacancy states.

Accurate and Effective Studies of Peptide Conformations and Protein-Peptide Interactions

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Abstract : Residue-specific force fields (RSFF) have been developed based on fitting the statistical free energy distributions of individual amino acid residues.[1,2] These force fields lead to promising description of peptides, especially cyclic peptides, and their interactions with proteins through molecular dynamics simulations.[3-5] A probability density reweighting method has been developed which can accurately convert the conformational free energy distributions obtained from high-temperature molecular dynamics simulations to those at any designated temperature.[6,7] The generation of large among structures and their relative free energies allows us to use deep learning methods to develop free energy functions to effectively study the conformations of peptides and their interactions with proteins.[8]

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Localized active spaces and quantum embedding for molecular and periodic systems

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Transition metal systems present a significant challenge in quantum chemistry owing to the near-degeneracy of d-shell electrons. We have addressed this challenge by introducing the localized active space (LAS) self-consistent field method. This approach factorizes a complete active space (CAS) wave function into localized active space wave function fragments, facilitating the reintroduction of correlation between fragments through LAS state interaction (LASSI).

I will outline our latest efforts to automate the LASSI method and its application to tri- and tetra-iron complexes [1]. Additionally, I will present advancements in density matrix embedding theory utilizing multireference solvers for the accurate calculation of valence and core excitations [2]. Finally, I will show that the LAS concept can be applied naturally to solid state phenomena by treating each unit cell as a molecular fragment, which provides a comprehensive basis for the study of charge and energy transfer in solids. [3].

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Non-adiabaticity from first principles: The exact factorization

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The adiabatic approximation, describing the molecular wave function as a single product of a Born-Oppenheimer state and a nuclear wave packet, is a corner stone of modern quantum chemistry. It not only makes computations feasible, it also provides an intuitive picture of many chemical processes. Yet, many fascinating phenomena appear outside the adiabatic regime. A prime example is the phenomenon of electronic decoherence, i.e. the loss of quantumness, well-known for its capacity of preventing genuine scalable quantum computing to this day. In this lecture a unified approach to non-adiabaticity, known as the *exact factorization*, will be presented. The approach starts from a formally exact representatation of the full electron-nuclear wave function as a product of a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude [1]. The equations of motion for the two factors provide an ideal starting point to develop efficient algorithms for the study of non-adiabatic phenomena. The successful prediction of laser-induced isomerization processes [2], the ab-initio description of decoherence [3], calculations of the molecular Berry phase [4] will demonstrate the power of the approach. We shall develop the concept of exact forces on the nuclei which involve time-dependent potential-energy surfaces and Berry-connection-type vector potentials [5]. A particular manifestation of the latter are current-induced forces in molecular junctions where the vibrational and rotational motion is determined by an intricate interplay between the “electron wind”and electronic friction [6].

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Multistate Density Functional Theory and Applications

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In this talk, I will introduce multistate density functional theory (MSDFT) of multiple electronic states, extending the Hohenberg-Kohn theorems for the ground state to any number of N eigenstates. For the subspace spanned by the lowest N eigenstates of a molecular system, the fundamental variable is a matrix density $\boldsymbol{D}(r)$, consisting of state and transition densities. Then, the Hamiltonian matrix projected to the Hilbert subspace is a matrix functional $H[\boldsymbol{D}(r)]$ of the matrix density $\boldsymbol{D}(r)$. It follows that for any N-dimensional trial matrix density $\boldsymbol{D}'(r)$,

$$tr\{H[\boldsymbol{D}'(r)]\} \geq tr\{H[\boldsymbol{D}(r)]\}$$

where the equal sign holds true when $\boldsymbol{D}'(r) = \boldsymbol{D}(r)$. Thus, it is of interest to note that a single variational minimization, followed by diagonalization of the Hamiltonian matrix functional $H[\boldsymbol{D}(r)]$, yields exactly all eigenvalues of these N states.

Computationally, the N-matrix density $\boldsymbol{D}(r)$ can be mapped to a set of auxiliary, multiconfigurational wave functions, which can be expressed in terms of no more than N^2 Slater determinants. Then, the corresponding correlation matrix functional can be defined. Importantly, by enforcing the symmetry of a Hilbert subspace, namely the subspace invariance property, we further establish that given the correlation functional for a single state, all elements of the correlation matrix functional for the entire N-dimensional subspace are uniquely determined.

The existence of an upper bound in the number of determinant configurations to exactly represent $\boldsymbol{D}(r)$ defines a minimal active space (MAS), and different computational procedures can be designed to construct the auxiliary wave functions, purely used to represent the N-matrix density $\boldsymbol{D}(r)$. I will present the computational method and application of MSDFT to excited-state energy-transfer processes in light-harvesting of photosystem II and in photoreceptor proteins, along with examples of valence and core-level excitations of both open-shell and closed-shell molecules.

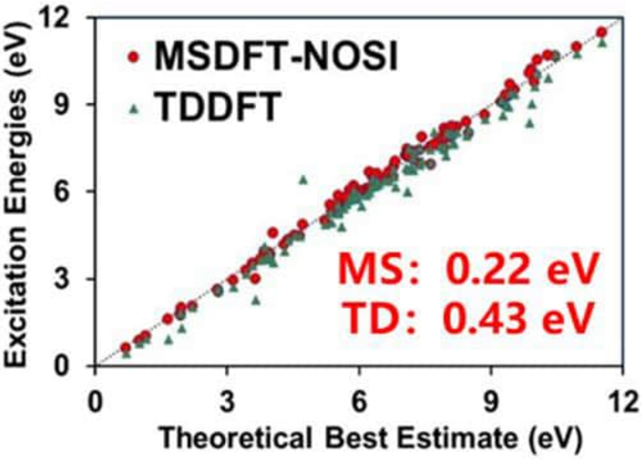

Fig. 1: Comparison of vertical excitation energies for 100 excited states determined by multistate density functional theory with nonorthogonal state interaction (MSDFT-NOSI) and time-dependent density functional theory (TDDFT) using the M06-2X functional and aug-cc-pVTZ basis set against the theoretical best estimates by Loos and coworkers. Root-of-mean-square errors are indicated in red.

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Spin adapted multireference correlation methods for construction of potential energy curves (PECs)

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In my talk, I will briefly explore the various ways our Unitary Group Adapted Multireference Coupled Cluster (UGA-MRCC) theories [1,2] and their perturbative versions (UGA-MRPT) [3,4] can be utilized in different interesting situations: (a) the study of interlacing and avoided crossing in a manifold of PECs of a given symmetry using a state-specific (SS) theory; (b) the comparison of a rigorous, reformulated UGA-SSMRCC equation with our previous approximate one and the effect on accuracy of the PECs; (c) a new UGA-MR formulation will be proposed to treat multiple states of a given space-spin symmetry at the same time.

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Classical Molecular Dynamics Simulations of Electronically Non-Adiabatic Processes

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A symmetrical quasi-classical (SQC) windowing methodology for classical trajectory simulations has been applied to the Meyer-Miller (MM) model for the electronic degrees of freedom in electronically non-adiabatic dynamics. The approach treats nuclear and electronic degrees of freedom (DOF) equivalently (i.e., by classical mechanics, thereby retaining the simplicity of standard molecular dynamics), providing ``quantization" of the electronic states through the symmetrical quasi-classical (SQC) windowing model. The approach is seen to be capable of treating extreme regimes of strong and weak coupling between the electronic states, as well as accurately describing coherence effects in the electronic DOF (including the de-coherence of such effects caused by coupling to the nuclear DOF). It is able to provide the full electronic density matrix from the one ensemble of trajectories, and the SQC windowing methodology correctly describes detailed balance (unlike the traditional Ehrenfest approach). Calculations can be (equivalently) carried out in the adiabatic or a diabatic representation of the electronic states, and it is shown that a modification of the canonical equations of motion in the adiabatic representation eliminates (without approximation) the need for second-derivative non-adiabatic coupling terms.

Breaking down the barrier between the quantum and classical worlds

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Quantum mechanics is hard – hard to simulate and often hard to interpret. I will discuss how we can design classical algorithms such that they give accurate predictions of certain quantum processes, while remaining simple and intuitive.

First, nonadiabatic ring-polymer instanton theory allows us to capture heavy-atom tunnelling using classical particles and anti-particles in imaginary time [1]. Recent developments have shown that singularities can appear in the flux correlation function, leading to a new type of transition-state theory with an infinite number of equally contributing mechanisms [2].

Second, the mapping approach to surface hopping [3] combines the best aspects of fewest-switches surface hopping (FSSH) with rigorous quasiclassical mapping methods to describe nonadiabatic transitions within a molecular dynamics framework. We show how it can be used to simulate rare events and explain why FSSH fails where MASH succeeds in capturing the correct Marcus behaviour [4].

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Nonadiabatic Field: A Conceptually New Approach for Nonadiabatic Dynamics

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Nonadiabatic transition dynamics lies at the core of many electron/hole transfer, photoactivated, and vacuum field-coupled processes. About a century after Ehrenfest proposed “Phasenraum” and the Ehrenfest theorem, we report a conceptually novel trajectory-based nonadiabatic dynamics approach, nonadiabatic field (NaF), based on a generalized exact coordinate–momentum phase space formulation of quantum mechanics, which includes U(F)/U(F-1) constraint phase space for electronic degrees of freedom (DOFs) and infinite phase space for nuclear DOFs. It does not employ the conventional Born–Oppenheimer or Ehrenfest trajectory in the nonadiabatic coupling region. Instead, in NaF the equations of motion of the independent trajectory involve a nonadiabatic nuclear force term in addition to an adiabatic nuclear force term of a single electronic state. A few benchmark tests for gas phase and condensed phase systems indicate that NaF offers a practical tool to capture the correct correlation of electronic and nuclear dynamics for processes where the states remain coupled all the time as well as for the asymptotic region where the coupling of electronic states vanishes.

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Small Matrix Path Integral Methods for Quantum Dynamics

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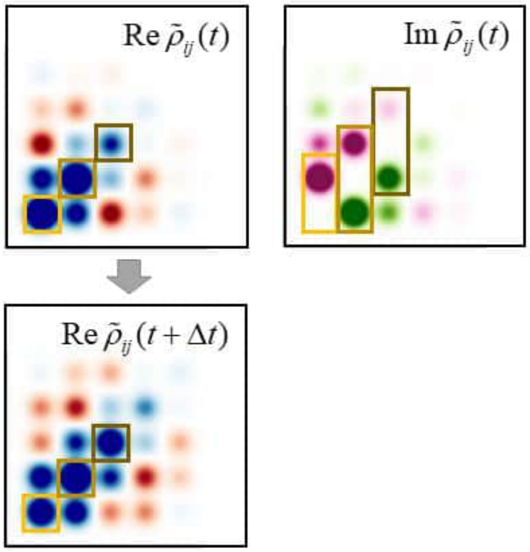
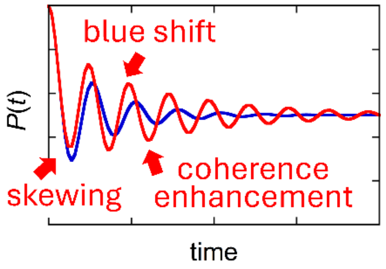
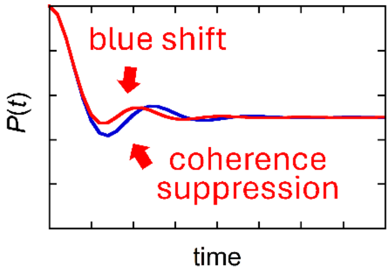
Since the early 1990s, the iterative quasi-adiabatic propagator path integral (QuAPI) methodology has enabled numerically exact, fully quantum mechanical simulation of dynamical properties for a small system coupled to a bath of harmonic oscillators, at zero or finite temperature. The QuAPI algorithm achieves linear scaling with the number of time steps by propagating a tensor that spans the memory interval, but the storage of QuAPI tensors effectively restricts application of the method to small systems and short or intermediate memory. Much recent effort has focused on the development of algorithms that reduce the storage requirements of QuAPI. In particular, recent work showed that one can further disentangle the path integral variables through the rigorous small matrix decomposition (SMatPI), which leads to expressions that involve matrices of size equal to that of the system's reduced density matrix (RDM), The SMatPI propagation matrices are obtained by evaluating path sums within the memory interval, which are accelerated through blip, kink, or other decompositions. The SMatPI algorithm eliminates tensor storage, enabling the simulation of long-memory processes and multistate systems.

Recent work has developed small matrix path integral decompositions for Hamiltonians that involve anharmonic baths, utilizing propagation matrices constructed by parsing the influence functional from the environment. The anh-SMatPI algorithm allows the exploration of novel effects induced by essential bath anharmonicity, which cannot be captured by effective harmonic bath mappings. These include skewed and blue-shifted population oscillations and enhanced or suppressed coherence.

Last, it has been shown that the time evolution of the full RDM encodes powerful information related to the amount of delocalization and instantaneous population derivatives. Coherence maps offer a powerful visualization tool for understanding the creation and destruction of quantum superpositions and enable a state-to-state pathway analysis of dynamical processes.







Quantum evolution represented by Brownian motion: Theory and applications

Jiushu Shao
Beijing Normal University

The exact quantum evolution is shown to be the ensemble average of random progresses described by a stochastic Schroedinger equation. In the stochastic formulation the momentum operator is coupled to a white Gaussian noise and thus the time evolution operator factorizes into two contributions due to the kinetic and the potential energies respectively. As the kinetic part is analytically solved, the quantum evolution is determined by the expectation of a stochastic amplitude resulting from the potential: The system moves with a constant velocity, subjected to a complex Brownian motion.

The stochastic representation of quantum evolution may provide flexible tools for studying quantum dynamics and thermodynamics. We will discuss how use it to derive propagators of some solvable systems. We will also show how to develop semiclassical approximations and Wigner-Kirkwood expansions.

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Simulation of quantum dynamics and transport using the hierarchical equations of motion method

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The hierarchical equations of motion (HEOM) formalism is an accurate and efficient approach to simulate the dynamics of open quantum systems [1]. Formulated as a density matrix scheme, it generalizes perturbative quantum master equations by including higher-order contributions as well as non-Markovian memory and allows for the systematic convergence of the results. In this talk, the formulation of the HEOM approach for molecular systems at metal surfaces is discussed, with a focus on the interaction of the molecular degrees of freedom with the electrons in the metal [2]. Employing a matrix-product state representation in twin space, larger molecular systems can be treated [3]. Furthermore, the use of the HEOM method to describe electronic friction is outlined [4]. Applications of the method are presented to simulate molecule-surface scattering, nonequilibrium reaction rates [5], as well as electron transport in molecular junctions [6].

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On the Stability of Path Integral Molecular Dynamics Simulations

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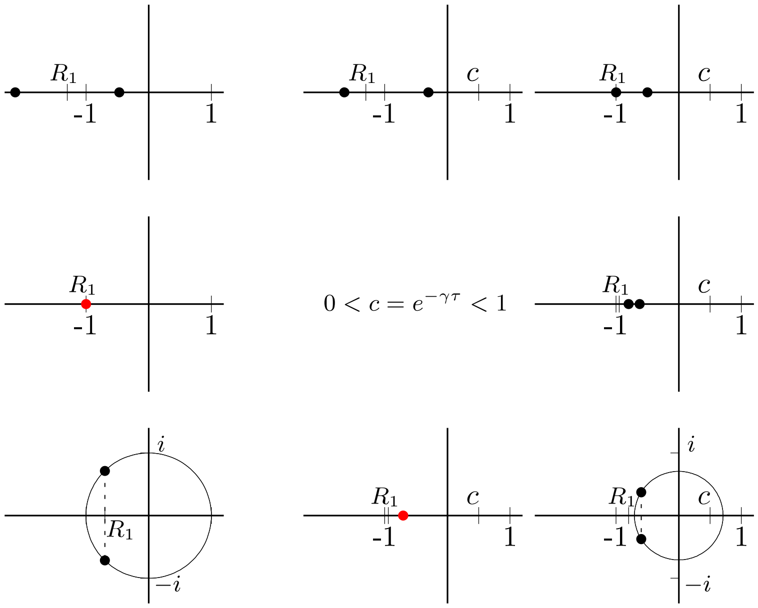
In this talk, we will discuss the stability of imaginary time path integral molecular dynamics simulations with or without coupling to a thermostat. The results are mostly based on an explicit understanding of the simple harmonic oscillator model in which the exact Hamiltonians associated with the discrete symplectic dynamics without a thermostat is solvable[1]. It is shown that the stability condition can be made free of any coupling strength such that a stable distribution can be always outputted from the simulations once certain symmetry conditions are satisfied.



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Ultrafast Dynamics on Many Electronic States

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Many important problems in chemistry and materials science involve nonadiabatic dynamics on large numbers of electronic states. Phenomena important for strong-field physics, energy conversion, hot carrier cooling, and relaxation of plasmonic excitations fall into this category. Some of these phenomena involve long lived coherences, which are challenging to accurately model with many mixed quantum-classical methods. We will present recent theoretical developments towards an accurate and broadly applicable simulation method for modeling dynamics in this regime. Specifically, we will present the development of the Ehrenfest with collapse to a block (TAB) method and a derivative designed for dense manifolds of states (DMS). The primary achievement of TAB-DMS is that it is able to accurately describe decoherence effects without requiring explicit computation of individual electronic eigenstates. Coupling to graphics processing unit accelerated time-dependent configuration interaction software to TAB and TAB-DMS enables ab initio nonadiabatic molecular dynamics simulations on many electronic states, in full nuclear dimensionality, and without prior knowledge of reaction mechanism. The utility of this approach will be demonstrated by application to long-lived electronic coherences observed in recent ultrafast experiments.

Global switching trajectory surface hopping molecular dynamics simulation with TDDFT potential energy surfaces

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In order to perform nonadiabatic molecular dynamic simulation for large photochemical systems, time-dependent density function theory (TDDFT) provides accurate ab. initio potential energy surfaces. Global switching algorithm does not need to calculate nonadiabatic coupling vectors. It was demonstrated that potential energy surfaces calculated by TDDFT with and without spin-flip can simulate quite similar answer for average quantities like quantum yields and lifetimes [1]. Furthermore, global switching trajectory surface hopping molecular dynamics simulation on ordinary TDDFT potential energy surfaces can correctly describe complicated conical intersection networks between the S_0 and S_1 for ultrafast photoisomerization of dMe-OMe-NAIP [2] and for retinal protonated Schiff-base photoisomerization [3]. Simulated quantum yields and lifetimes agree well with experimental measurements.

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Nonadiabatic Dynamics, Time-Resolved Pump-Probe Spectra and Machine Learnings

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Abstract:

Nonadiabatic dynamics widely exist in photophysics, photochemistry and photobiology. We tried to develop theoretical approaches to study the photoinduced nonadiabatic dynamics.

As time-resolved spectroscopy is a very important tool to study the ultrafast dynamics, it is necessary to simulate these spectral signals for the understanding of the experimental observations. We combined the doorway-window representation of the nonlinear response theories and ab initio nonadiabatic dynamics to simulate various time-resolved pump-probe spectra, including transient absorption spectra, time-resolved fluorescence spectra and two-dimensional electronic spectra. We also combine the trajectory surface hopping dynamics and the elastic scattering theory to simulate the ultrafast electronic diffraction signals.

We tried to combine deep leaning method and numerical accurate quantum dynamics approach to simulate the long-time quantum evolution of open quantum system. This approach allows us to obtain the evolution of reduced density matrix of open quantum system with a low computational cost. It demonstrates that the deep learning approach is the important tool to speed up the long-time quantum evolution. The similar time-series analysis tool can also be used to propagate all nuclear and electronic degrees of freedom in the trajectory evolution of the SQC-MM dynamics.

Can classical simulations sense conical intersections?

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Conical intersections (CI) provide fast energy relaxation from electronic excited states. About 10 years ago, Hamm and Stock [Phys. Rev. Lett. 109, 173201 (2012)] demonstrated the presence of CI's for purely vibrational potential energy surfaces and fast vibrational energy relaxation due to these CI's. This leads to the question: can molecular dynamics simulations capture the effects of these CI's, or are quantum nuclear effects important? We answer this question using simple model potentials and comparing classical simulations with quantum simulations, along with some semiclassical simulations. To our surprise, we find that classical simulations agree with the exact quantum simulations better than semiclassical simulations.

Design principles for functionals based on systematic expansions

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Density Functional Theory encounters a great success, but the development of new functionals is an ongoing challenge. In particular, routes to design functionals with controllable precision and in a systematic way are still needed. We propose to use perturbation theory around the homogeneous electron gas in a way that is optimized using physical insight, and to combine it with the recently developed connector approach [1,2] in order to satisfy an exact limit. In particular, we develop an explicit density functional for the Kohn-Sham exchange correlation potential. The self-consistently calculated charge density and potential compare well with numerically exact results of auxiliary field Quantum Monte Carlo calculations for bulk silicon, sodium chloride, and copper [3,4], better than results from some standard density functionals. Directions for further improvement are discussed.

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Unveiling the Origins of DFT Errors in Open-Shell d- and f-Electron Compounds: An Analysis of SCAN's Performance in Addressing Self-Interaction Error and Strong Correlation, with Enhanced SIE Reduction within Semilocal Approximations

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Compounds with open-shell d- and f-electrons, often exhibiting exotic properties and dubbed as correlated materials characterized by a strong inter-electronic Hubbard U, present great challenges to density functional theory (DFT), one of the most widely used electronic structure theories. DFT in principle is exact for the ground state total energy, while its exchange correlation energy has to be approximated in practice. There are two major error sources in a DFT calculation for correlated materials: 1) the strong correlation (SC) originating from a degeneracy or near-degeneracy closely related to Hubbard U, for example, the near-degeneracy of the partially filled d-subshells, and 2) the self-interaction error (SIE) due to the imperfect cancellation of the spurious classical Coulomb interaction between an electron and itself. In this talk, I will show that, without explicitly involving Hubbard U, the strongly-constrained and appropriately-normed (SCAN) density functional [1] gives significantly improved descriptions of the structural, energetic, electronic, and magnetic properties of correlated materials, including transition metal monoxides [2], high-Tc cuprate superconductors [3,4], and SmB6 [5], previously believed to be inaccessible to DFT. I will further explain the reasons behind SCAN's improvement, showing its reduction in SIE and the help from spin symmetry breaking if SC is present. In addition, I will discuss the persistent challenge of SIE in modern density functional approximations, typically illustrated using the prototypical one-electron system H2+. While efforts to eliminate SIE through computationally expensive nonlocal density functionals have been ongoing, it is equally crucial to investigate whether SIE can be mitigated within more efficient semilocal density functional frameworks. Our study introduces a non-empirical meta-generalized gradient approximation (meta-GGA) that incorporates the Laplacian of the electron density, showing significant SIE reduction and an improved binding energy curve for H2+ across a broad range of bond lengths. This approach not only builds on the success of SCAN but also opens avenues for further advancements within semilocal density functional approximations, enhancing the accuracy and applicability of DFT in modeling correlated materials. Outlooks on further improving density functionals for correlated materials will be discussed.

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Constrained Nuclear-Electronic Orbital (CNEO) Framework: Describing Hydrogen-Related Chemistry with Energy Surfaces Incorporating Nuclear Quantum Effects

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Nuclear quantum effects play a crucial role in various chemical and biological processes, but accurately incorporating them into large-scale molecular simulations remains challenging. Recently, we developed a new quantum chemistry and molecular dynamics framework called constrained nuclear-electronic orbital (CNEO) framework,[1,2] which enables the accurate and efficient inclusion of nuclear quantum effects in quantum chemistry calculations and molecular dynamics simulations. Using CNEO molecular dynamics (CNEO-MD),[3] we calculated the vibrational spectra of a series of molecular systems and found that it significantly outperforms conventional ab initio molecular dynamics (AIMD), especially for vibrational modes characterized by substantial hydrogen motion.[3–5] Moreover, by integrating the CNEO framework with transition state theory (TST), we demonstrated that the resulting CNEO-TST significantly outperforms conventional TST in predicting hydrogen transfer reaction rate constants, while maintaining a similar computational cost. Additionally, our recent development of CNEO excited-state theories and CNEO hybrid quantum mechanics/molecular mechanics (QM/MM) approaches demonstrated the strong potential of the CNEO framework for accurately describing nuclear quantum effects in more complex chemical processes and biological systems.

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Machine-learning-accelerated photodynamics simulations in complex environments towards new materials and medicines

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Photochemical reactions are increasingly important for constructing value-added, strained organic architectures. Direct excitation and photoredox reactions typically require mild conditions to access therapeutic gases (e.g., carbon monoxide) and new synthetic methodologies. *A priori* design of photochemical reactions is challenging because degenerate excited states often result in competing reaction mechanisms to undesired products. Further, a lack of experimental techniques that provide atomistic structural information on ultrafast timescales (10^{-15} – 10^{-12} s) has limited general rules about these reactions. Computations, however, provide a path forward. I will discuss how my group has leveraged multiconfigurational complete active space self consistent field (CASSCF) calculations, non-adiabatic molecular dynamics, and machine learning (ML) techniques to understand reaction mechanisms and enumerate new reaction pathways. I will introduce our new open-access machine learning tool, Python Rapid Artificial Intelligence *Ab Initio* Molecular Dynamics (PyRAI^{2}MD), which enables 100,000-fold longer simulations than current NAMD simulations with multiconfigurational quantum chemical methods. I will describe how PyRAI^{2}MD has enabled the first ML-NAMD simulations with QM (CAS/HF) training data. The presentation will explain the origins of the reactivities and selectivities of photochemical pericyclic reactions and CO-evolving reactions in aqueous environments.

Deep learning model for predicting optical properties of organic molecules in solutions

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Reliable prediction of the molecular properties of organic compounds is crucial for developing new organic materials in various research fields such as, organic solar cells, organic light-emitting diodes (OLEDs), bio-imaging, organic sensors, and organic dyes. In particular, the optical properties, such as absorption and emission peak positions and bandwidths, extinction coefficients, photoluminescence quantum yield (PLQY), and emission lifetime, are important for the development of chromophores and fluorophores. Recently, we have developed deep learning (DL) models using an experimental database to predict the optical properties of organic compounds in various local environments [1]. We built an experimental database by collecting related data of organic compounds from the literature [2]. Our experimental database includes ~28,000 unique organic chromophores in 409 solvents or solid states, yielding ~80,000 chromophore/solvent combinations. Our DL models include the chromophore–solvent interaction to account for the effect of local environments on the optical properties. Our DL models based on our experimental database were found to reliably and quickly predict the aforementioned properties of organic compounds in solution, gas phase, film, and powder. Our DL models can be efficiently used for developing the component materials in optoelectronic devices including OLEDs and organic solar cells in combined with combinatorial enumeration.

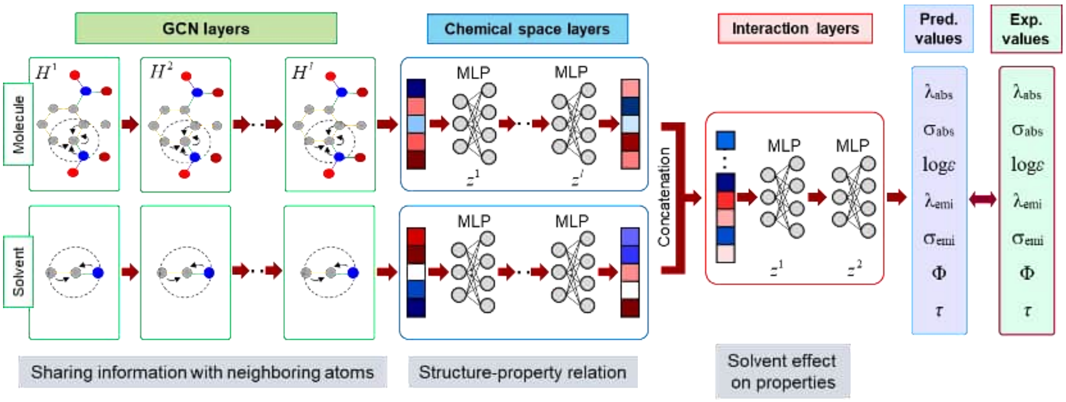

Figure 1. Deep learning model to predict optical properties of organic molecules in solutions.

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Machine Learning for Quantum Dissipative Dynamics

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Accurate simulations of quantum dynamics in complex condensed-phase systems are our gateway to understanding many physical, chemical, and biological processes. Exact numerical simulations often require computational resources that scale exponentially with the number of simulated time steps and the size of the system. Approximate perturbative or quantum-classical methods are often only reliable at short simulation times, rendering such methods inapplicable to study long-time quantum phenomena. I will present several methods for simulating long-time dynamics of dissipative quantum systems, including physics-based and machine-learning-based approaches [1,2]. Specifically, I will show how many different types of machine learning models including artificial neural networks and kernel ridge regression models can efficiently and accurately simulate complex quantum dynamics across different regimes. Best models considerably reduce the required computational time for long-time simulations with no compromise in accuracy providing new routes for simulating quantum dynamics for arbitrarily long times, starting with computationally feasible short-time dynamical information.

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Recent Progress in Neural Network-based Quantum Monte Carlo

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Abstract:

Quantum Monte Carlo (QMC) methods have long been a powerful tool in computational quantum science. In recent years, the integration of neural networks into QMC has opened up exciting new possibilities. Neural network based QMC leverages the expressive power of neural networks, resulting in better representation of quantum states. In this talk, I will introduce the fundamentals of Variational Monte Carlo (VMC), a real-space QMC approach, and demonstrate how neural networks can improve its performance in solving complex many-body quantum problems. I will also discuss recent advancements, including efficiency improvements and excited state calculations.

Bio:

Weiluo Ren is currently a research scientist at ByteDance Research, specializing in AI for Science. He holds a Ph.D. from Stanford University and a bachelor's degree from the University of Science and Technology of China. His research focuses on Neural Network based Quantum Monte Carlo methods and their applications in quantum physics and chemistry.

Block-correlated Coupled Cluster Methods for Strongly Correlated Systems

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I will report our recent advances in developing electronic structure methods for strongly correlated systems. With the generalized valence bond (GVB) wave function as the reference function, we have developed block-correlated coupled cluster method (GVB-BCCC in short) at the *ab initio* level for strongly correlated systems.[1,2] The GVB-BCCC method in its present form is demonstrated to provide accurate descriptions for static correlation in strongly correlated systems. Our calculations on a number of typical systems have shown that GVB-BCCC4 (with up to four-pair correlation) can provide nearly exact ground-state energies as the density matrix renormalization group (DMRG) method for systems with large active spaces.[3] An equation-of-motion GVB-BCCC method (EOM-GVB-BCCC) was developed to describe low-lying excited states for strongly correlated systems.[4] The EOM-GVB-BCCC2b method with up to two-pair correlation has been implemented. Test calculations for a few strongly correlated systems have demonstarted that the S-T gaps from this method are quite consistent with the DMRG results. These results show that GVB-BCCC and EOM-GVB-BCCC are expected to be practical theoretical tools for ground-state and excited state calculations of strongly correlated systems with large active spaces.

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Quantum chemistry methods to study strongly correlated systems – from variational to machine learning approaches

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Polyaromatic hydrocarbons (PAHs) such as acenes have long been studied due to its interesting optical properties and low singlet triplet gaps. Earlier studies[1] have already noticed that use of complete valence active space is imperative to the understanding of its qualitative and quantitative properties. We have used density matrix renormalization group (DMRG).[2] Further small modification to the PAH topology shows interesting new phases of behaviour in its optical gaps. We have understood the effect of these effects based on spin frustration due to the presence of odd membered rings. In this talk, I will discuss these observations from molecular and model Hamiltonian perspectives.[3]

Further developments based on artificial neural network based configuration interaction for strongly correlated systems will also be discussed.[4] The similarities between the ANNs and the MPS wavefunctions will be leveraged for 2D systems.

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New quantum chemical approaches based on renormalized modes/states for large strongly correlated systems

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To quantitatively characterize realistic strongly correlated systems, it is essential to efficiently consider the non-uniform interactions between different sites and the interaction between the embedded active subsystem and the remaining correlated environment. To achieve this, we recently introduced several new post- density matrix normalization group (DMRG) and time-dependent DMRG (TD-DMRG) approaches. These include: (1) Renormalized residue-based multi-reference configuration interaction (RR-MRCI), which enhances the computational accuracy and efficiency of internally contracted (ic) MRCI by renormalizing the contracted bases with small-sized buffer environments consisting of a few external orbitals as probes. (2) Hierarchical mapping (HM)-TD-DMRG, which reduces a large environment to a small number of renormalized environmental modes that account for the most crucial system-environment interactions through stepwise mapping transformation. (3) Block interaction product state (BIPS)-DMRG, which offers a low-scaling fragment-based method for large correlated systems. These advances extend the efficacy of highly accurate DMRG/TD-DMRG computations to the quantitative characterization of the electronic structure and quantum dynamics in realistic strongly correlated systems.

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Beyond the Dailey-Townes model: chemical information from the electric field gradient

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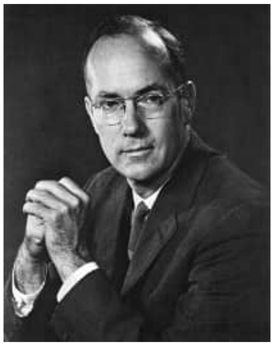
Benjamin Peter Dailey (1919 - 2021)



Charles Hard Townes (1915 – 2015)

In 1935 Schüler and Schmidt reported clear deviations from the Landé interval rule, associated with the nuclear magnetic dipole moment, in the hyperfine splittings of the atomic spectra of the two naturally occurring isotopes of europium, ^{151}Eu and ^{153}Eu, both with nuclear spin $I = 5/2$. They suggested that this observation could be explained by an ellipsoid shape of the nucleus [1]. The underlying theory was subsequently worked out by Casimir [2,3]. The interaction energy is generally given by

$$E_Q = -\frac{1}{3}\sum_{ij}\Theta_{ij}E^{[1]}_{i;j};\quad E^{[1]}_{i;j} = \left.\frac{\partial E_i}{\partial r_j}\right|_{\boldsymbol{r}=\boldsymbol{a}},$$

where Θ_{ij} is a component of the traceless nuclear electric quadrupole moment and $E^{[1]}_{i;j}$ a component of the electric field gradient at the nuclear position $\boldsymbol{a}$. For atoms and linear molecules, the interaction energy associated with nuclear spin state $|I, m_I\rangle$ can be expressed as [4]

$$E_Q\left(I, m_I\right) = \frac{e^2qQ}{4I\left(2I-1\right)}\left[3m_I^2 - I\left(I+1\right)\right],$$

where the electric quadrupole moment Q of the nucleus is defined as $eQ = 2\Theta_{zz}$ and the electric field gradient q is defined as $eq = -E^{[1]}_{z;z}$. Accurate electronic structure calculations of the electric field gradient combined with experiment allows the extraction of the nuclear quadrupole moment Q [5].

However, it was pointed out already in 1949 by Townes and Dailey that the electric field gradient at the nuclear position is a sensitive probe of bonding in molecules, since it vanishes in the case of spherical symmetry [6]. In the present contribution [7] we exploit and extend the Dailey-Townes model using the projection analysis [8] implemented in the DIRAC program for relativistic molecular calculations [9].

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Developing Local Quantum Vibration Embedding Framework for Multi-dimensional Vibrational Spectra

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Vibrational spectroscopy is crucial for studying molecular vibrations, but fully quantum-mechanical spectral simulations are limited to systems with few degrees of freedom, while classical approximations do not fully capture quantum effects. High-precision methods like Local Quantum Vibration Embedding (LQVE) address this by selectively applying quantum mechanics to key vibrations and using classical methods for the rest, thus balancing accuracy and computational cost [1, 2]. LQVE is adaptable, allowing researchers to customize it to their specific needs. Recently, we have attempted to apply LQVE to intramolecular resonance problems in multidimensional spectra. Using the aLQVH@LQVE method, we can simultaneously solve for multidimensional anharmonic oscillators. To address the issue of rapidly increasing computational cost in multiple dimensions, we further incorporated machine learning methods [2]. The results are in good agreement with experimental data. To address vibrational mode errors in instantaneous environments, we developed a controlled roto-translational constraint optimization method. Additionally, we created a similar method for molecular dynamics to explore rotationally related ion transport mechanisms in battery materials [3].

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The Behaviors of Molecules in Strong Coupling Regimes

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When few(many) molecules are placed in a nano(micro) cavity, the photon quasiparticles in the cavity will greatly enhance the light-matter interactions, leading to the generation of molecular polaritons and the modification of molecular photophysical and photochemical behaviors. To fully understand the precise mechanisms underpinning polaritonic chemistry and provide a deeper understanding of the underlying quantum mechanical processes, building useful theoretical models and advanced computational frameworks to describe and predict the behavior of these hybrid states is crucial but challenged. Here I report my group's two recent works on understanding the molecular polariton-mediated phenomena and dynamics. The first one is about the development and application of a hybrid RT-TDDFT/RT-ωFQ scheme, which combines the real-time time-dependent density functional theory (RT-TDDFT) approach and time-domain frequency dependent fluctuating charge (TD-ωFQ) mode, to effectively simulate the plasmon-mediated "real-time" electronic dynamics and even the coupled electron-nuclear dynamics in both the weak and strong coupling regimes. The other is about the development of the advanced analytical energy derivative approaches within the framework of the cavity Born-Oppenheimer density functional theory to efficiently calculate the vibro-polaritonic spectra and explore the critical points on the cavity potential energy surface.

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Role of Metal-Oxide Interfaces in Catalysis

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Our understanding of metal-oxide interactions in applied catalysts remains limited due to the challenging nature of such studies. In this talk, I will discuss how the combination of cutting-edge simulations and experiments can shed light on the activity of metal-oxide interfaces in various catalysts. Often nanoparticle-support interactions improve the activity of catalysts due to the altered binding energies of reaction intermediates at the boundary of the nanoparticle-support interface [1], e.g. in Pd/ZrO_2 catalysts for CO oxidation [2]. The catalytic activity may also be increased by the spillover of the reacting species through the metal-oxide interface, e.g., in Pd-promoted $ZnZrO_x$ catalysts for methanol synthesis [4]. The rate of H spillover in these catalysts can be further improved by engineering a distribution network for H* within the catalyst in the form of carbon nanotubes supporting Pd nanoparticles [5].

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Heterogenous Catalysis by Interpretable Machine Learning

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How metals interact with gaseous reactants and support underneath, *i.e.*, metal-reactant interactions and metal-support interactions, are two cornerstones of supported metal catalysts. Metal-reactant interaction (MRI) determines activity and selectivity, where the nature of the active sites and their structure sensitivity are the keys to rational design of efficient catalysts but have been debated for almost one century in heterogeneous catalysis. While metal-support interaction (MSI) is vital in stabilizing dispersed catalysts and impacting a variety of interfacial processes, but developing a fundamental theory has been challenging because of the intricate interfaces. To address these challenges, here, we harness the power of interpretable machine learning, domain knowledge, theoretical and experimental data to establish a general theory of MRI and MSI grounded in topological under-coordinated number, metal-metal interaction and metal-oxygen interaction. It is physical and concise, providing a constructive strategy to understand the structure sensitivity, decipher the entangled geometric and electronic effects, and transferable to metal-on-oxide and oxide-on-metal interfaces. The theory reveals that metallophilicity dominates support effects and suboxide encapsulation over metal nanoparticles. A principle of strong metallophilicity for encapsulation occurrence is thus proposed and substantiated by extensive experiments, resolving the longstanding debates around strong MSI. The theory paves the way to engineer the interfacial processes for advanced metal catalysts.

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Simulations in electrocatalysis

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I will discuss our recent advances in the modeling of materials that can achieve CO2 conversion electrochemically. Starting by the fundamentals I will discuss the changes in the materials under true reaction conditions and how these affect the reactivity and the selectivity of the catalytic processes.

Data-driven symbiosis between computations & experiments for electrochemical reactions

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Electrochemistry holds the promise to be a cornerstone for the sustainable production of fuels and chemicals. However, these catalytic reactions are increasingly complex to understand and hereby also improve. In particular reactions that suffers from selectivity challenges such as CO_2 reduction

In this talk, I will discuss how experiments and computational simulations can support each other. I will focus on electrochemical reduction of NO_x, CO_2, N_2, and the combinations. Importantly, all these reactions share a direct competition with hydrogen, and furthermore, several products are formed from each reactant of these reactants. I will give minimalistic models that do not overfit or over interpretating experimental data. Examples are:

i) Electrochemical CO_2 reduction show multiple different products depending on metal catalyst [1]. I will show why copper is unique as catalyst with a multiple-carbon product distribution [2]. Following I will discuss data analytics on copper facets to steer the product distribution [3].

ii) Electrochemical NO_x reduction, also multiple products are formed; N_2O, N_2 and NH_3[4]. Several catalyst enable reductions to ammonia amongst them copper [5] and recently also Co and Fe based catalysts close to their reduction potential [6].

iii) Electrochemical N_2 reduction to ammonia (NH_3) at ambient conditions is burgeoning [7-8]. Most interesting in aqueous there is not a “copper” catalyst [9]. While in non-aqueous, the univocally working system is a Li-mediate system [10]. For this system, I will show that varying multiple experimental parameters display similar performance characteristics [11] and I will discuss systems beyond lithium.

Finally, I will discuss how one can use these insights to establish predictive schemes for products beyond the typical reduction reaction products, hereunder synthesis of urea [12-13].

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Modeling electrocatalytic interfaces via advanced DFT calculations

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Electrocatalytic systems are crucial in various renewable energy conversion and storage technologies, forming a foundational basis for our sustainable future. Realizing their full potential requires advancements in catalytic materials to achieve better catalytic efficiencies, higher stability, and lower costs. This necessitates an atomic-level understanding of electrocatalytic systems, particularly the complex electrocatalyst-electrolyte interface, which involves numerous components and processes. Moreover, the interface properties can vary substantially depending on solvent and electrode potential and the variations can, in turn, have direct impact on electrocatalytic behaviour.

The grand-canonical ensemble (GCE) DFT calculations [1] offer a robust framework for modelling electrochemical interfaces and reactions at the atomic level, while maintaining fixed electrode potentials. In my presentation, I will cover our recent developments in GCE-DFT [2], which make the method applicable to systems beyond the reach of the standard GCE-DFT approach. The examples of GCE-DFT calculations to be presented include computing Pourbaix diagrams for metals under realistic reaction conditions [3] demonstrating how pH and potential can strongly influence the state of the catalyst and the electro-oxidation of biomass-derived species [3,4].

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Condition-Dependent Energy Landscape of Catalytic Paths for Activity and Stability Control

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Countering catalyst inhibition in homogeneous hydrogenation is challenging due to the scaling relation between the inhibited and active states of the catalyst. Recently we demonstrated common additives act as environmental promotors allowing to selectively suppress the product inhibition the metal-ligand cooperative hydrogenation catalysts.[1-4] In this lecture I will discuss the origin of these phenomena and highlight the critical importance of the environmental effects on the intrinsic reactivity of realistic catalyst systems. Our combined experimental and computational studies reveal that the thermodynamic landscape of the competing reaction paths including inhibitory equilibria exhibits a non-monotonic dependence on the concentration of the base additive [2,3]. We demonstrate that under idealized conditions at low concentration base additives modulate the ionic strength. In a realistic catalyst system with high concentrations, the promotor speciation changes resulting in substantial perturbations to the free energy of catalytic paths, ultimately deciding its fate. Environment modulation is a practical tool for controlling the longevity and sustainability of noble metal catalyst as we demonstrate by bringing Ru-catalyzed ester and bicarbonate hydrogenation processes from merely lab curiosities to the industrial applications.

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Atomically Precise Heterogeneous Catalysis with Graphdiyne-Supported Metal Clusters

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Single-atom catalysts (SACs) have achieved great success in the past decade[1,2]. As a natural extension, single-cluster catalysts (SCCs) become a new frontier to extend the applications of SACs that feature simplistic single-atom active centers.[3-5] SCCs with precise numbers of atoms and structural configurations possess SAC's merits, yet have greater potentials for catalyzing complex reactions and/or bulky reactants. The recently synthesized graphdiyne materials featuring natural holes for anchoring metal cluster is an ideal substrate for SCCs[4]. In this talk, we will discuss the stability and catalytic performance of single atom catalysts and *n*-atom SCCs ($n = 2, 3, 4$). Through systematic quantum-chemical studies and computational screening, we report the rational design of transition metal clusters M_x ($x = 2, 3, 4$) anchored on graphdiyne as a novel kind of stable SCCs with great potentials for efficient and precise heterogenous catalysis. Examples will be given on the catalytic performance for hydrogenation of alkynes, nitrogen reduction reaction (NRR), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), CO_2 reduction reactions (CO2RR) and C-X (X = C, N, O, S) coupling reactions.[4,5] These graphdiyne supported SCCs provide an ideal benchmark scaffold for rational design of atomically precise heterogeneous catalysts (APCat) for industrially important chemical reactions.

Keywords: graphdiyne；single-cluster catalyst；single-atom catalysis; computational modeling

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Density Functional Theory Studies for CO_2 Conversion to value-added chemicals

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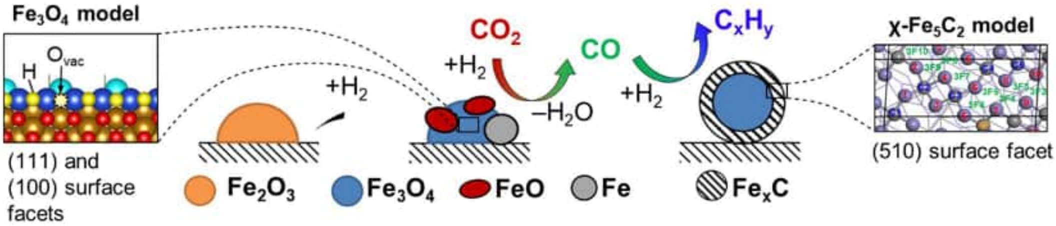
Computational modelling is a powerful tool to understand reaction mechanism and provide insights in rational catalyst design. In recent years, we have worked in a variety of areas from thermal catalysis to electrocatalysis; from transitional metal surface to organic molecule modified surface; from metal oxide to metal carbide catalyst. Currently, our catalysis research focuses on topics associated with the transition to low carbon future. In this talk, I will give an overview of the catalysis research in our group and showcase some of our recent research work in CO_2 utilization. For example, I will discuss the Modified Fischer-Tropsch (MFT) process, which is a promising method for converting CO_2 into chemicals. The Fe-based catalyst is typically used for the MFT reaction, and the dynamic state of the catalyst observed in experiments reveals the complexity of the catalytic system. Thus, it is a big challenge to obtain a deep understanding of the whole chemical process, including the catalyst deactivation and regeneration.[1,2] In this work, we explored the underlying reaction mechanisms in MFT reactions. For example, we proposed a novel mechanism for CO-derived surface C hydrogenation to ethylene using density functional theory (DFT) simulations. Our approach considers previously unexplored surface diffusion of partially hydrogenated intermediates (CH, CHCH), significantly reducing the effective energy barrier.[1] The insights into iron catalyst evolution during CO_2 reduction and F-T reaction over iron carbide surface shed some light on the development of strategies for achieving efficient catalyst performance.



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Recent advances in divide-and-conquer quantum chemistry: toward large scale and beyond

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We have developed a linear-scaling divide-and-conquer (DC) quantum chemical method [1], which was originally proposed by Yang and coworkers [2]. In this presentation, we will review the method especially focusing on the recent advances such as the automatic determination of the buffer region [3], the combination with the GFN-xTB method [4], and the DC-based periodic boundary condition (PBC) calculation for HF and MP2 theories. Furthermore, we will report on our current research combining the DC method with quantum computation, such as the variational quantum eigensolver (VQE), and discuss the prospects for high-precision large-scale calculations using quantum computers.

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Fragment molecular orbital calculations for biomolecules

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The fragment molecular orbital (FMO) method is a theoretical method that enables quantum chemical calculations of whole bio-macromolecules, such as proteins and nucleic acids, yielding the interaction energies between fragments in addition to the energies and electron densities of the whole molecules [1-3]. The FMO calculations of protein complexes that have been structurally analyzed experimentally allow for quantitative analysis and physicochemical interpretation of intra- and intermolecular interactions within the complexes. Combined with classical molecular dynamics simulations, predictive analysis of protein structures and interactions, including mutants, taking into account thermal fluctuations in water can be performed, and with experimental verification a deeper understanding of life science phenomena can be obtained. Here we describe the "structure and interaction basis" obtained through the complementary use of experimental structure and the theoretical calculations.

The results of our FMO calculations to date can be obtained and analyzed from the FMO database [4], and as of the end of August 2024, 37,450 structures have been made publicly available (https://drugdesign.riken.jp/FMODB/).

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Bootstrap Embedding

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Bootstrap embedding (BE) is a recently developed quantum fragment embedding method that approximates a large system as a collection of *overlapping* fragments. By matching fragments in the overlap region and using only information gleaned from the core of a given fragment, BE show rapid and essentially monotonic convergence as the fragment size increases. In particular, we have demonstrated that BE works well for: strongly correlated systems; for large systems containing ~10,000 basis functions; extended basis sets; and periodic systems in one and two dimensions. In all cases, with appropriately chosen fragments, BE is able to recover ~99.8% of the total correlation energy from the parent method. We will discuss future prospects, including the use of novel fragment solvers, inclusion of non-bonded interactions and the possibility of novel boundary conditions relevant to molecular impurities at surfaces.

Density matrix embedding theory: A density (matrix) functional perspective

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Density matrix embedding theory (DMET) [1] is a relatively recent quantum embedding approach to strongly correlated electrons that applies not only to materials but also to molecules. Its key feature is the drastic reduction in system size it offers, through the design of a one-electron quantum bath subspace, for evaluating local electron correlations. Its current practical implementation raises many fundamental questions. Some of them will be addressed in this presentation. The first one is about the one-electron nature of the bath. Is there a (static) route for improving or even exactifying its construction in the context of one-electron reduced density matrix (1RDM) functional theory, for example [2,3]? As we will see, a similar question arises when extending DMET to an ensemble of ground and low-lying excited states [3]. Another important point is the self-consistent optimization of the bath. While using the 1RDM as basic variable leads to an ill-conditioned problem, turning to its diagonal elements instead (which can be seen as the density in a localized orbital basis) offers the possibility to formally exactify DMET from the perspective of Kohn-Sham density functional theory, as embodied in the local potential functional embedding theory (LPFET) [4,5].

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Orthogonal and non-orthogonal local orbitals based quantum embedding approach to strongly correlated systems

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Electronic structure theory for strongly correlated systems (SCSs) poses a long-standing challenge in molecular quantum chemistry and condensed matter theory. Complete active space self-consistent field (CASSCF) theory has played a particularly important role in ab initio treatment of SCSs, but can not be directly applied to extended systems like solids and surfaces. There are continuous efforts in developing various quantum embedding techniques to treat complex strongly correlated systems accurately and efficiently. Density-matrix embedding theory (DMET), formulated in terms of the Schmidt decomposition of Slater determinant wave-functions, provides a systematic framework to combine low- and high-level quantum chemistry methods to treat strongly correlated systems. In this work, we first developed an efficient quantum embedding approach in the DMET framework that uses restricted open-shell Hartree-Fock (ROHF) as the low-level solver, and the CASSCF plus subsequent state interaction treatment of spin–orbit coupling (CASSI-SO) as the high-level solver, which are found to be able to predict accurately zero-field splitting parameters in typical 3d and 4f single-ion magnets (SIMs) with significantly reduced computational cost compared to its all-electron counterpart [1]. While the standard DMET relies on the partition of the whole system in terms of orthogonal localized orbitals, we further generalize DMET to the partition of the system in terms of non-orthogonal local orbitals, which can be used to achieve DMET-like quantum embedding with greater flexibility and efficiency, and little loss of accuracy [2].

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Exploration of the Optical Properties of Point Defects in Semiconductors and Insulators using Time-dependent Density Functional Theory and Quantum Embedding Methods

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A robust description of excited states for complex heterogeneous systems is needed to model optically activated processes in materials. We focus on simulations of point defects in diamond and silicon carbide, which are of interest for the realization of quantum technologies. We present a formulation of spin-conserving and spin-flip TDDFT, including the calculation of analytical forces, which allows for efficient calculations of excited state properties of solid-state systems with hundreds to thousands of atoms [1-2]. To include a description of double excitations we use full configuration interaction (FCI) embedded in DFT+GW [3]. These examples benefit from the use of the latest developments in high-performance computing architectures, which include pre-exascale capable machines [4] and quantum processors [5].

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Computer-Aided Nanoscience Research: Nanoice, Superhydrophobicity, and Topological Wetting State

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In this talk I shall report several research findings from my group, including: (1) Prediction of new phases of two-dimensional nano-ice and ice clathrate, and one-dimensional helical ice. (2) Superhydrophobic phenomena at the nanoscale. I will show a molecular-dynamics video to demonstrate the “Lotus effect” at nanoscale. (3) Topological wetting states at nano- and micro-scales. In these studies, tools of computational chemistry, including classical molecular dynamics and ab initio molecular dynamics simulations are employed. Some of these theoretical findings are later confirmed by experiments, such as the first 2D ice in nature, and the first 1D ice nanotube in nature.[1-4]

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Machine Learning Material Design and Synthesis for Small Datasets

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Machine learning algorithms offer new opportunities and challenges for the development of new materials. One of the key challenges currently faced by data-driven material design is the lack of high-quality material data, referred to as the "small dataset" problem. This not only seriously affects the accuracy of data-driven models but also greatly limits their applicable scenarios. In this report, I will discuss the feasibility and challenges of advanced machine learning algorithms such as active learning and transfer learning to address "small dataset" problem: i) We developed an active learning framework to efficiently search the chemical space through edge sampling, and successfully screened more than 30 room-temperature 2D ferromagnetic materials from 200,000 candidates; ii) By incorporating adversarial generative model with expert knowledge, we have realized the transfer learning from 3D effective mass to 2D mobility, and successfully predicted out more than 20 high-mobility 2D semiconductor materials. Additionally, I will demonstrate how we combine small-batch high-throughput experiments, prior expert knowledge, and machine learning algorithms to enhance the synthesizability of new materials.

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Deriving catalyst design strategies from computational data using artificial intelligence

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Despite the accelerating progress in technology in recent years, only a small fraction of possible functional materials for various applications have been explored so far. One of the reasons for the slow exploration of materials space is the extreme complexity of the relation between the atomic composition of a material and its functional properties. Moreover, traditional computational approaches with high predictive power, such as density-functional theory and other first-principles methods, remain too demanding to directly explore the vast materials space. We demonstrate how to bridge the materials-space complexity with an artificial-intelligence (AI) approach called subgroup discovery (SGD) for an example from electrocatalysis. We have developed this approach to identify combinations of a catalytic material's features (catalyst's genes) that result in optimal catalytic properties. The approach is applied to understand and design novel catalysts for oxygen evolution reaction (OER) based on transition-metal-organic frameworks [1]. Based on physical understanding of SGD subgroups, we demonstrate why only a combination of material's features can result in a good catalytic performance in case of complex reactions with several intermediates. The design strategy discovered by AI allowed us to find an exceptionally efficient catalyst whose performance and stability were confirmed experimentally.

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Approaching Larger Spatial and Temporal Scales in Polymer Simulations

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Due to large molecular size and slow relaxation of polymer chains, a great amount of issues related to long-distance chain displacement, such as phase separation and self-assembly, cannot be tackled easily with conventional molecular dynamic simulations. We need to use coarse-grained polymer models to solve problems commonly encountered in (bio)polymer morphology and pattern formation. We have developed coarse-grained methods suitable for describing interaction between polymers, as well as stochastic reaction model for use in coarse-grained simulations via combining molecular dynamics and Monte Carlo to especially study the influences of chemical reactions on the construction of nanostructures. We have also developed GPU-accelerated molecular simulation software for use in coarse-grained simulations of polymer systems with several unique simulation tools developed by us [1]. In this talk, I will introduce key features of above-mentioned simulation techniques, together with representative applications.

[1] http://pygamd.com .

Fast Quantum Chemistry on Multi-GPU Architectures: Achievements and Future Directions

Giuseppe Barca

Quantum chemical modelling has become an indispensable tool in the discovery and design of new materials, drugs, catalysts, and other critical compounds. This progress is underpinned by the continuous evolution of computational quantum chemistry methods and the high-performance computing systems that they use.

As we enter the exascale computing era, the landscape of high-performance computing is shifting from traditional CPU-centric architectures to those dominated by accelerators, particularly GPUs. To harness the full potential of this transformation, quantum chemical methods must evolve in tandem, enabling the simulation of larger and more intricate molecular systems with unprecedented speed and precision. This transition represents a critical juncture in computational chemistry, where the fusion of cutting-edge hardware with algorithmic innovation will dictate future advancements.

In this presentation, I will introduce the EXtreme-scale Electronic Structure System (EXESS), a novel quantum chemistry package designed from the group up to efficiently exploit the computational power of multi-GPU architectures. EXESS achieves unparalleled performance in key quantum chemical computations, including Resolution of Identity Hartree-Fock (RI-HF), Hartree-Fock (HF), and Resolution of Identity MP2 (RI-MP2) energy and gradient calculations, as well as microcanonical ensemble Ab Initio Molecular Dynamics (AIMD). Compared to established CPU-based codes like ORCA and Q-Chem, EXESS delivers speedups ranging from two to over three orders of magnitude in time-to-solution.

I will explore the challenges and milestones encountered in the development of algorithms and software optimized for the world’s most powerful supercomputers. Additionally, I will discuss record-breaking calculations performed using EXESS on over 34,000 GPUs on the Frontier supercomputer. These calculations broke the exaflop barrier for the first time in quantum chemistry enabling AIMD/RI-MP2 simulations at the biomolecular scales required for quantum-accurate computer aided drug discovery.

“Chemical reactions” between HPC/AI and RGs

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The RGs, i.e. the Renormalization Group methods with the key idea of basis transformation, are emerging as powerful quantum chemical tools with their own characteristics. For example, the real-space RG (RSRG) can be adapted as the fragmentation approach for describing the low-lying states for larger molecules, and the density-matrix RG (DMRG) can be treated as the upward substitution for the popular active-space solver (e.g. CAS) in multi-reference (MR) calculations.

Herein, we will talk about our recent works about applying HPC/AI technique in the calculating process of RG-based approaches, as well as some explores about RG-inspired machine-learning/quantum machine-learning (ML/QML) process. I.e.,

1. On the one side, the ML-assisted load prediction, [1] static/dynamic scheduling optimization, [1] and coded fault-tolerance [2] are introduced into the fragment-based Renormalized Exciton Method (REM), aiming for the fail-safe automatic high-throughput calculations of low-lying states.
2. On the other side, the GPU-accelerated Reduced Density Matrix (RDM) [3] and (externally contracted) MR Configuration Interactions (MRCI) [4] computational frameworks are developed, in order to accelerate the post-DMRG calculations, e.g. DMRG-cu(4)-NEVPT2 and DMRG2sCI-MRCI.
3. Besides that, imitating and upon the construction process of Bloch’s effective Hamiltonian in RSRG, a quantum state-based neural-network (QSNN) model is proposed and used in anomaly detection together with China Unicom, in which both classical and quantum solvers are explored. [5]

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Discontinuous Galerkin Hartree-Fock calculations for predicting accurate electronic structures of mesoscopic-scale metal-semiconductor junctions with millions of atoms

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The evaluation of the exact Hartree-Fock exchange in hybrid density functional theory (DFT) is a crucial ingredient for accurately predicting electronic structures in molecules and solids. However, its application is currently limited to 5K atoms on leadership supercomputers due to its ultra-high computational complexity O(N^4). Herein, we propose a new discontinuous Galerkin Hartree-Fock (DGHF) method for large-scale hybrid functional electronic structure calculations. We present a massively parallel DGHF implementation on exascale supercomputers to reduce the high computational scaling of constructing the HFX matrix from O(N^4) to O(N). We showcase how DGHF can be used to predict accurate electronic structures of complex metal-semiconductor junctions with 2.5M atoms (17.2M electrons) using 35.9M cores on exascale Sunway supercomputer. This is the first time high-accuracy hybrid functional electronic structure calculations enable us to simulate next-generation electronic devices at mesoscopic scale (200 nm).

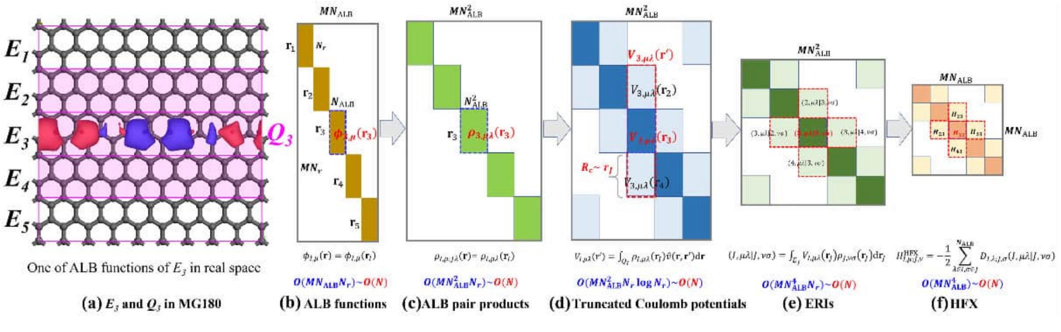

Figure 1. The key spirit of constructing the HFX matrix in DGHF.

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Molecular response under highly confined electromagnetic fields

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The creation of plasmonic nanocavity provides a powerful tool to break the conventional diffraction limit of light, enabling to achieve experimentally ultrahigh spatial resolution of molecular Raman image. The strong spatial confinement effect of plasmonic field has challenged the conventional molecular response theory, as widely adopted plan wave approximation for the light is no longer applicable. In this talk, I will briefly introduce our generalized molecular response theory in the framework of effective field Hamiltonian (EFH) [1], which allows to efficiently take all characteristics of localized plasmonic fields into consideration. In combination with first principles simulations, it can quantitatively reproduce state-of-the-art experimental observations, revealing the underlying intrinsic physics and mechanisms. The predictive power of EFH is demonstrated by several new phenomena generated from its peculiar spatial, momentum, time, and energy structures. The corresponding experimental verifications are also briefly described.

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Modeling paramagnetic NMR.

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The paramagnetic NMR (pNMR) chemical shift of a given nucleus is the difference between the observed shift and the shift observed for a diamagnetic analogue. This shift may be split into a dipolar term, arising from the magnetic dipolar interaction between the metal center and the NMR active nucleus, and a contact term, due to the spin delocalization leaking from the paramagnetic center towards the ligand [1].

The calculations of the pNMR shifts with first principle methods are either based on a EPR spin Hamiltonian, on magnetic susceptibility tensor or directly, based on a sum over state formalism [2]. We will analyze the connection between the three approaches, with particular emphasis on the role of the spin-orbit coupling.

The first approach will be illustrated by a first-row transition metal complexes [3] and the second one, by actinide complexes, where spin-orbit coupling is important. It gives access to the anisotropic magnetic susceptibility $\Delta\chi$ to the spin density at the nuclei of the ligands, and consequently to the ligand hyperfine coupling constants. The pathway of the spin density from the magnetic 5f orbitals to the nuclei will be discussed [4] .

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VeloxChem: Science and education-enabling platform for quantum molecular modeling

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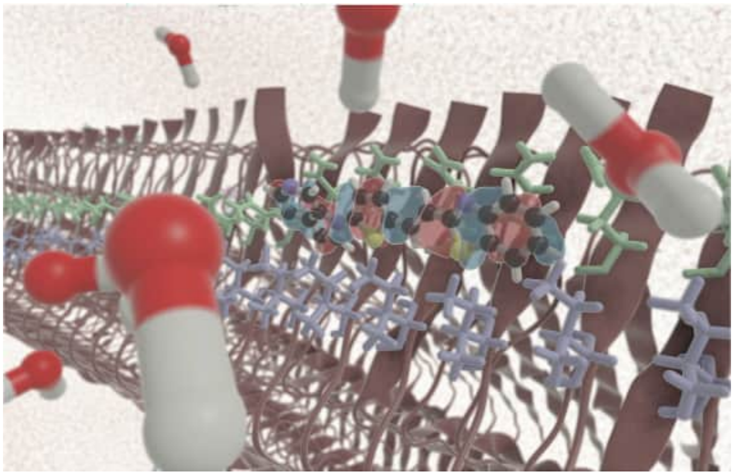
VeloxChem[1] is a science- and educational-enabling software platform for quantum molecular modeling at the levels of DFT and TDDFT. It is strictly object-oriented and written in a hybrid of the Python and C++/CUDA/HIP programming languages and it implements extremely efficient parallelism through MPI and OpenMP. Noteworthy functionalities include real and complex response functions up to cubic order with geometric derivatives of complex linear response functions to enable resonance Raman spectrum simulations and built-in interoperability with classical molecular dynamics simulations by means of an automatized force-field generation. It installs with conda on Windows/macOS/Linux personal computers as well as it can harness the power of modern supercomputers with GPU hardware acceleration.

Largely based on VeloxChem is the eChem[2] Jupyter book initiative that allows for interactive deep learning of the theory and methods in theoretical chemistry. The Jupyter notebooks upon which this electronic book is built present theory and numerical methods with intertwined illustrative Python code cells. In addition to this educational aspect, we find notebooks to be useful for code prototyping as a means to accelerate the process of software development.



The VIAMD[3] graphical user interface enables visual interactive analysis of the complex molecular systems that VeloxChem can address, including the electronic structures of ground and excited states together with the associated transition densities.

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Chemical dynamics from the hierarchical equations of motion method: Methodology developments and applications

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In recent years, the hierarchical equations of motion (HEOM) method has developed into a instrumental tool for investigating quantum dynamics in condensed phases. To overcome the difficulties presented by more complex system-environment couplings and low-temperature simulations, we have enhanced the computational efficiency of the HEOM by incorporating tensor network methods and novel spectral decomposition techniques. Additionally, we demonstrate recent applications of the HEOM in areas such as charge transport and nonadiabatic dynamics on metal surfaces.

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Disentangling spectroscopic signals with trajectory surface-hopping methods based on vibronic coupling methods

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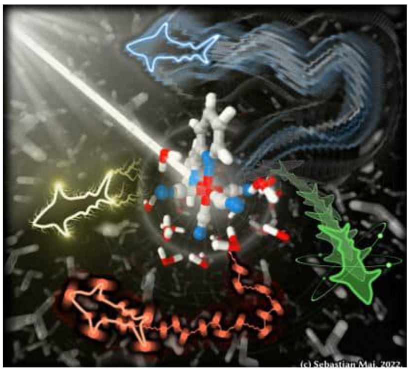
Understanding complex molecular dynamics following photoexcitation is essential for interpreting time-resolved spectroscopic signals. However, in systems with a large number of electronic and nuclear degrees of freedom, spectroscopic signals often become convoluted, making it challenging to isolate the contributions from different relaxation pathways and electronic states. Here we demonstrate the efficiency of trajectory surface hopping methods based on vibronic coupling models [1] to aid the interpretation of time-resolved femtosecond spectroscopic experiments. Through a series of examples, we demonstrate how these approaches extend the applicability of excited-state dynamics to longer time scales than what is typically achievable with on-the-fly methods. Additionally, by incorporating multiscale approaches [2], we provide an efficient and comprehensive framework to capture the influence of the environment on excited-state dynamics [3].



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Exact Ab Initio Conical Intersection Dynamics

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Conical intersections are ubiquitous in polyatomic molecules and responsible for a wide range of phenomena in photochemistry and photophysics. Here, we introduce an ab initio discrete variable local diabatic representation (LDR) for the numerically exact correlated electron-nuclear dynamics around conical intersections [1, 2, 3]. The LDR can be considered a generalization of the crude adiabatic representation with many reference geometries. It directly employs the adiabatic electronic states without adiabatic-to-diabatic transformation but avoids the divergence of the first and second derivative couplings at degeneracy points. We further show it is robust to the random gauge choices of the electronic wavefunction phases. It captures all nonadiabatic effects, including nonradiative transitions, electronic coherence, and geometric phases.

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Electronic decay process spectra including nuclear degrees of freedom

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In the field of chemistry, where nuclear motion has traditionally been a focal point, we now explore the ultra-rapid electronic motion spanning attoseconds to femtoseconds, demonstrating that it is equally integral and relevant to the discipline. The advent of ultrashort attosecond pulse technology has revolutionized our ability to directly observe electronic rearrangements in atoms and molecules, offering a time-resolved insight into these swift processes. Prominent examples include Auger-Meitner decay and Interparticle Coulombic Decay (ICD). However, the real challenge lies in interpreting these observations, where theoretical models are indispensable.

Building upon the analytical framework introduced in Phys. Rev. A 101, 043414 (2020), which analyzed the spectra of electrons emitted during electronic decay processes from a purely electronic perspective, our paper represents a significant advancement. We extend this theoretical base to include nuclear dynamics, utilizing the Born-Oppenheimer approximation to deepen our under- standing of the intricate interaction between electronic and nuclear motion in these processes.

We illustrate the impact of incorporating nuclear degrees of freedom in several theoretical cases characterized by different numbers of vibrational bound states in both the electronic resonance and the electronic final state. This approach not only clarifies complex spectral features and unusual peak shapes but also demonstrates a method for extracting the energy differences between multiple vibrational resonance states through their distinctive interference patterns.

MARVEL, SNAPS, and hubs

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Apart from few-body problems, first-principles quantum-chemical computations, with or without the Born–Oppenheimer approximation, are unable to come even close to the accuracy of rovibrational spectroscopic measurements. To help experimentalists designing and assessing their measurements, the field of graph or network theory, that is discrete mathematics, comes to the rescue. Briefly, in the case of high-resolution spectroscopy, one can rely only on the validity of the Ritz principle, providing discreteness for both the transitions and the energy levels. Consequently, a spectroscopic network, a graph $G(V,E)$, can be formed from the results of high-resolution spectroscopic measurements, whereby the vertices V are the quantum states, and the edges E are the transitions connecting them. The degree distribution of spectroscopic networks built upon measurement results is similar to those of most complex human networks (*e.g.*, the internet, social networks, and air traffic): it is characterized by a few vertices with very large degree counts, called hubs, and a lot of vertices with just a few degrees (thus, quantum mechanics also builds an almost scale-free network). The network view of spectroscopic measurements [1] led to the development of a special tool, called MARVEL, standing for Measured Active Rotational-Vibrational Energy Levels, which helps not only to analyze high-resolution spectra of molecules but also the improvement of large spectroscopic line-by-line databases, like HITRAN. Using the MARVEL approach one can invert the direct spectroscopic information and come up with empirical energy levels with well-defined uncertainties, reflecting the accuracy of the measurements. These empirical (MARVEL) energy levels allow the representation of all the measurements made for a given molecule and, furtermore, they can predict transitions with experimental accuracy. The spectroscopic-network approach can also be used to select target lines for precision-spectroscopy measurements, where the measurement of each line still takes a considerable effort. Thanks to SNAPS (Spectroscopic-Network-Assisted Precision Spectroscopy) [2] and related measurements, hubs of several water isotopol-ogues as well as of parent acetylene have become known with kHz accuracy.

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Harnessing Chemical Understanding with Wave Function Theory, Density Functional Theory, Machine Learning, and Quantum Computers

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In this talk, we overview the status of how theory and computation can be exploited to obtain chemical understanding from wave function theory and density functional theory, and then outlook the likely impact of machine learning (ML) and quantum computers (QC) to appreciate traditional chemical concepts. It is maintained that the development and maturation of ML and QC methods in theoretical and computational chemistry represent two paradigm shifts about how the Schrödinger equation can be solved. New chemical understanding can be harnessed in these two new paradigms by making respective use of ML features and QC qubits. Before that happens, however, we still have hurdles to face and obstacles to overcome in both ML and QC arenas. Possible pathways to tackle these challenges are proposed. We anticipate that hierarchical modeling, in contrast to multiscale modeling, will emerge and thrive, becoming the workhorse of in silico simulations in the next few decades.

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Frontier Electron Density to Characterize the Molecular Interaction and Reactivity

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It is an active research field of the theoretical chemistry to characterize the molecular structures and properties and to explore the interaction and reactivity between molecules. In the density functional theory, the electron density is used to express and deduce the molecular properties.[1] We have proposed the concept and method of the frontier electron density (FED)[2,3]. We define the two-dimensional characteristic molecular contour which is unique and intrinsic based on the one electron potential. The contour is the set of the points at which the one-electron potential equals to the negative value of the first ionization potential of the molecule, called molecular intrinsic characteristic contour (MICC). The electron density on the MICC is called the frontier electron density (FED). The steric force on the MICC is also called the frontier steric force (FSF). The ab initio method is used to calculate the FED and FSF of the molecules by using our own program. Figure 1 displays frontier electron density (left) and frontier steric force (right) which have been used to explore the regioselectivity and stereoselectivity of tert-butylbenzene. We have explored the relationship of the strengths and sites between molecules with their extremes.

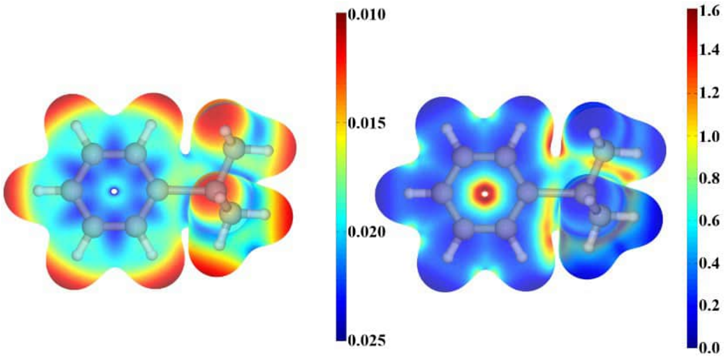

Figure 1. The regioselectivity and stereoselectivity of tert-butylbenzene. Frontier electron density (left); Frontier steric force (right)

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Acknowledgments

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Efficiently learning activation energies with ML models augmented with Valence Bond reactivity theory derived descriptors

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Recent advances in machine learning (ML) and computational chemistry have opened the door to the development of hybrid computational workflows for reaction screening and discovery.[1] Unfortunately, conventional ML algorithms tend to be extremely data hungry, and generating extensive (computational) reactivity datasets is tedious and computationally expensive. Additionally, the resulting trained models tend to be poorly generalizable. In this talk, I will discuss how introducing domain knowledge about chemical reactivity theories can dramatically improve the data efficiency, as well as the ability to generalize, of ML models.

As a proof of concept, I will focus on hydrogen atom transfer reactions, and I will demonstrate that Valence Bond reactivity theory can be used to construct an informative and transferable representation for these reactions.[2] Importantly, the identified set of descriptors constituting this VB-inspired representation do not need to be computed explicitly but can be predicted on-the-fly by repurposing existing quantum chemical descriptor datasets found in the literature, with the help of a surrogate model. In this manner, extremely fast, data-efficient and versatile ML workflows can be set up, and I will demonstrate that meaningful predictions can be made for datasets as small as a few hundred data points, or even smaller, with the developed approach.

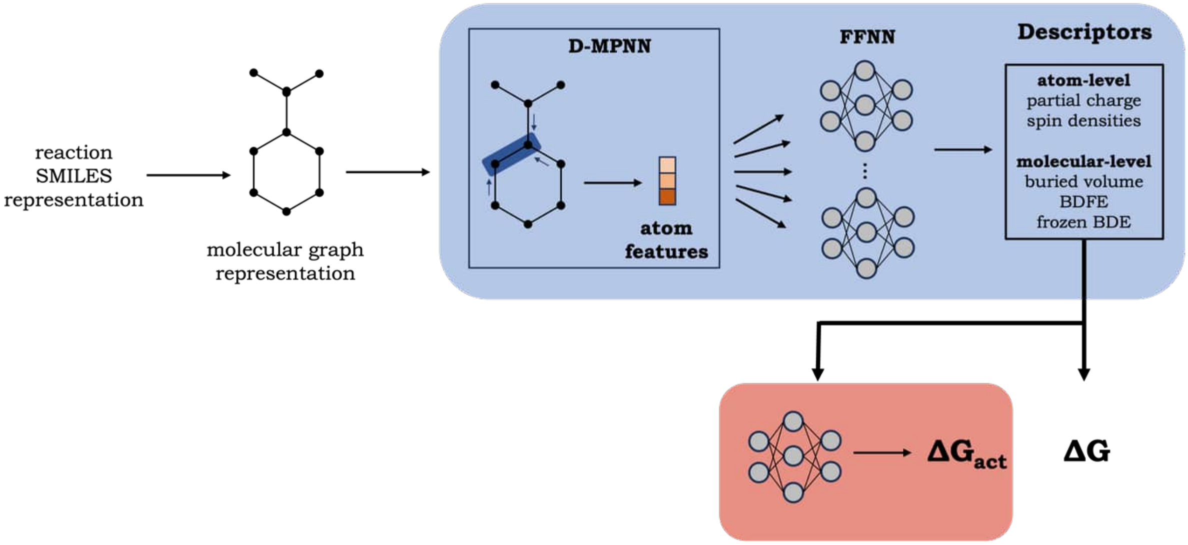

Fig. 1. An overview of the developed ML workflow for reactivity prediction of hydrogen atom transfer reactions.

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Analysis of allostery in a transcription factor using molecular simulations and machine learning

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While allostery has been a topic of intense interest for the past several decades, our understanding of the underlying mechanism at the molecular level continues to be challenged by new experimental observations. Specifically, a recent deep mutational scanning study of a bacterial transcription factor TetR found that allostery hotspot residues are broadly distributed over a major portion of the protein structure, rather than being clustered near the ligand-binding and DNA-binding domain interfaces as often discussed in structure-based studies. Similarly, loss of inducibility due to mutation of hotspots could be rescued by additional mutations that were also broadly distributed throughout the protein. These findings suggest that the contributions of hotspot residues are unlikely explained by a single mechanism, thus calling for different analysis strategies compared to previous computational studies. In this seminar, I'll discuss our recent efforts that integrated atomistic simulations, machine learning analysis and a thermodynamic (MWC like) model to explain the various aspects of the experimental findings. The key realization from these analyses is that allostery hotspots may contribute by either mediating inter-domain communications or intra-domain energetics. The mechanistic insights we gleaned for TetR might be broadly applicable to allosteric systems with the similar structural topology.

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Characterization of Intrinsic Disorder in Actin-Binding LIM Protein 1

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The heart adjusts to its workload through various mechanisms, including chemical changes to proteins that control cell contraction. Many of these changes, like phosphorylation and ubiquitination, occur in unstructured parts of proteins, called intrinsically disordered regions (IDRs). However, understanding how these modifications affect the whole protein and myofilament has been challenging. Since heart problems often involve major shifts in these chemical modifications, especially in IDRs, studying their effects is crucial. We proposed that changes in myofilament protein ABLIM1 are regulated by its IDRs, where phosphorylation alters their shape and ability to bind to other proteins. To test this, we used molecular simulations to see how ABLIM1's structure changes before and after phosphorylation. Our results suggest that phosphorylation changes ABLIM1's properties, potentially affecting how it interacts with other targets, like titin, by altering its effective concentration. These findings offer new insights into how myofilament proteins are regulated through chemical modifications.

Integrative biophysics of ERalpha allosteric interactions and disruption

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The estrogen receptor (ER or ERalpha) is a key driver of breast cancer. However, the allosteric interactions between its DNA-binding domain (DBD) and ligand-binding domain (LBD) have long remained elusive, impeding the development of novel therapeutic strategies.

Using advanced integrative biophysics via data-driven computations, we uncovered a previously uncharacterized allosteric channel facilitating hormonal signal transmission between these domains (*Nature Communications* 2018). This discovery was rigorously validated through site-directed mutagenesis and cellular ER activity assays. Leveraging these insights, we developed an innovative drug discovery platform targeting the ER domain interface (*US Patent* 16/695,487, issued in 2024), leading to the identification of mitoxantrone (MTO) as a potent binder to this unexplored domain interface.

To elucidate MTO's mechanism of action, we implemented a multidisciplinary strategy: computational docking and umbrella sampling simulations predicted MTO's binding to the DBD-LBD interface. Site-directed mutagenesis and biophysical assays confirmed the predicted binding. Biochemical studies revealed MTO-induced conformational changes in ER. Cellular investigations demonstrated that MTO rapidly alters ER subcellular localization, promotes degradation, uniquely modulates ER-targeted gene expression, and potently inhibits ER-mediated transcription, cell growth, and tumor progression (bioRxiv, 2024).

Our work represents two significant advancements: (1) the first characterization of highly flexible ER DBD-LBD interactions, providing crucial insights into ER function and allostery, and (2) the first proof of concept for targeting the ER DBD-LBD interface with small molecule disruptors to modulate ER-mediated function.

These findings underscore the power of integrative biophysics and computational modeling in advancing both basic science and translational therapeutics. They also highlight the need for further in-depth biophysical investigations to fully harness this fundamental structure-function-intervention approach in combating ER-driven breast cancer.

Searching for Less Entangled Orbitals

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Quantum entanglement makes efficiently describing the electronic structure of molecules challenging on classical computers. In this talk, I will introduce an algorithm to search for less entangled orbitals (LEOs) with the help of density matrix renormalization group (DMRG) algorithm. On one hand, this method allows us to identify genuine challenging systems with strong multiconfigurational characters. On the other hand, the resulting LEOs can be used in quantum computation, which can potentially increase the success probability of quantum phase estimation and alleviate computational resources in variational quantum computation.

Toward Perturbation Theory Methods on Quantum Computers

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Perturbation theory, used in a wide range of fields, is a powerful tool for approximate solutions to complex problems, starting from the exact solution of a related, simpler problem. Advances in quantum computing, especially over the past several years, provide opportunities for alternatives to classical methods. Here, we present a general quantum circuit estimating both the energy and eigenstates corrections that is far superior to the classical version when estimating second-order energy corrections. We demonstrate our approach as applied to the two-site extended Hubbard model. In addition to numerical simulations based on qiskit, results on IBM's quantum hardware are also presented. Our work offers a general approach to studying complex systems with quantum devices, with no training or optimization process needed to obtain the perturbative terms, which can be generalized to other Hamiltonian systems both in chemistry and physics.

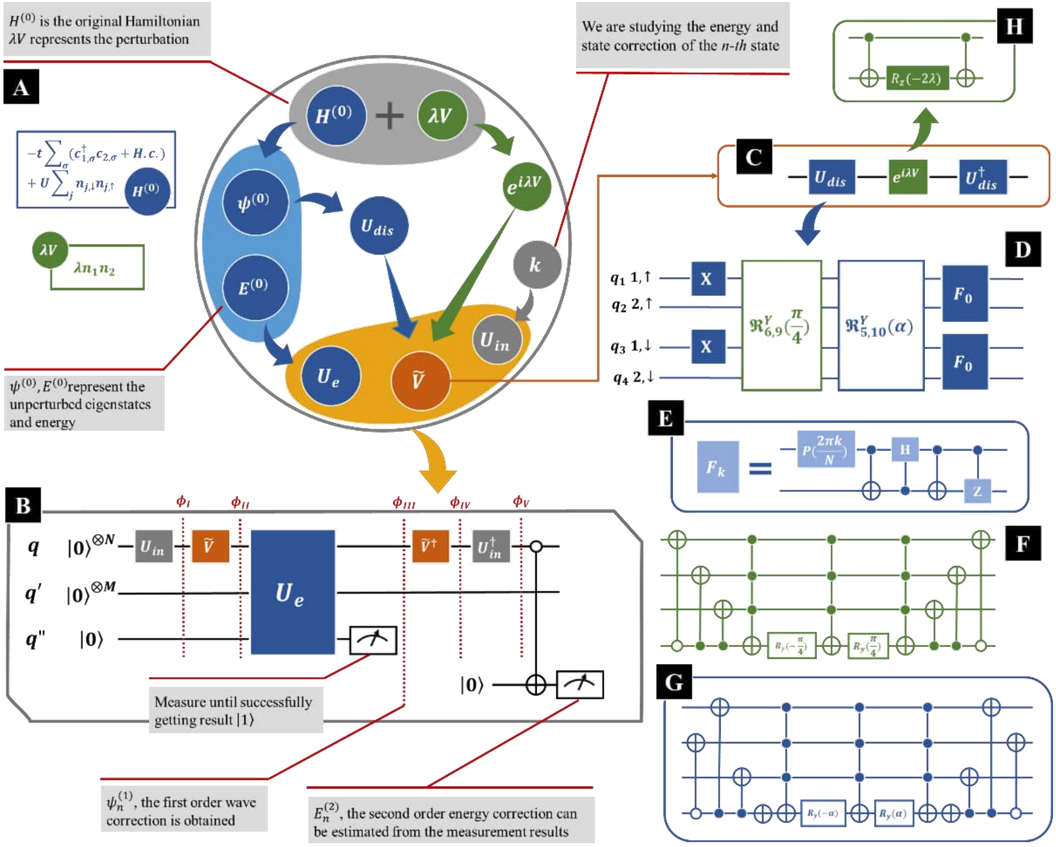

Figure 1. Scheme of the quantum circuit implementation.

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Beyond energy: Expanding quantum Monte Carlo with derivatives

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We illustrate here how we can obtain accurate derivatives in quantum Monte Carlo (QMC) for the optimization of variational and structural parameters in the ground and excited states. For several challenging molecules, we demonstrate the excellent performance of our protocol in the computation of excitation energies and structures even at the simpler variational Monte Carlo level. We then discuss the impact of computing the interatomic forces within diffusion Monte Carlo and investigate the quality of machine-learning force fields trained on these forces, using simple fluxional molecules in the ground state as prototypical case.

Stochastic Approaches to Quantum Chemistry

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Stochastic approaches to quantum chemistry are characterised by an element of random selection in the process of solving usually an electronic structure problem, and as such energies and properties also carry an error bar and these are often dependent on the precise details of the stochastic approach. In contrasted, deterministic approaches, while still somewhat dependent on choices for initialization, can often come to numerical results to machine precision.

In quantum chemistry, stochastic approaches, owing to often being far

from black-box and relatively expensive, often occupy a specialist niche of benchmarking. In particular, Variational and Diffusion Monte Carlo, Full Configuration Interaction Quantum Monte Carlo (FCIQMC) [1] and Coupled Cluster Monte Carlo (CCMC) [2,3], and selected CI approaches fall into this category.

In this talk, I discuss the differences in approach, applicability and success of these stochastic approaches, and present new developments in propagators, making use of a Chebyshev projector [4] which enhances the convergence properties of FCIQMC and CCMC, and explore how stochastic approaches can be used in conjunction with emerging quantum computing applications [5].

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Exploiting Non-Abelian Point-Group Symmetry to Estimate the Exact Ground-State Correlation Energy of Benzene in a Polarized Split-Valence Triple-Zeta Basis Set

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Local electronic-structure methods in quantum chemistry operate on the ability to compress electron correlations more efficiently in a basis of spatially localized molecular orbitals than in a parent set of canonical orbitals. However, many typical choices of localized orbitals tend to be related by selected, near-exact symmetry operations whenever a molecule belongs to a point group, a feature which remains largely unexploited in most local correlation methods. In this talk, I will demonstrate how to leverage a recent unitary protocol for enforcing symmetry properties among localized orbitals [1] to yield a high-accuracy estimate of the exact ground-state correlation energy of benzene (D_{6h}) in correlation-consistent polarized basis sets of both double- and triple-ζ quality [2]. Through an initial application to many-body expanded full configuration interaction (MBE-FCI) theory [3-5], we show how molecular point-group symmetry can lead to computational savings that are inversely proportional to the order of the point group in a manner generally applicable to the acceleration of modern local correlation methods [6]. In combination with an efficient clustering of orbitals [7], the developments reported here considerably improve upon the computational efficacy of MBE-FCI.

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Towards a quantitatively accurate universal potential for water

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Water exhibits many anomalous properties, which has given rise to uninterrupted interest in it. Numerous theoretical models have been proposed to elucidate the unique behavior of water across all phases, but the long-sought "universal water model" capable of describing the properties of water under different thermodynamic conditions remains elusive. In this talk, we will present a new potential energy surface (PES) of water by fitting many-body interaction energies from high-level electronic structure calculations by using fundamental invariants neural networks (FI-NN) in an unprecedented accuracy. With inclusions of up to four-body interaction energies with sufficient large cut-off distances, the simulated structural, thermodynamic, and dynamical properties of water clusters and bulk water using the new PES are uniformly in excellent agreement with the experimental observations without any empirical long-range potentials, indicating the long-sought "universal water model" is finally emerging

An MCTDH collocation method with more points than basis functions: obviating integrals

Robert Wodraszka, Jesse Simmons, and Tucker Carrington, *Queen's University, Kingston, Canada.*

It is common to use variational methods to solve the Schroedinger equation to study the motion of nuclei in a molecule or a reacting system. MCTDH is a variational method that uses optimized basis functions. When using a variational method, one must confront the problem of computing the matrices that are fed into whatever method is used to solve the Schroedinger equation, e.g. MCTDH. Many variational methods therefore require that the PES has a simple form that facilitates the calculation of the potential matrix. Most MCTDH calculations are done with a sum-of-products PES. In this talk, I shall present collocation ideas that obviate the need to compute the matrices required in a variational method. Like a variational method, a collocation method represents solutions as linear combinations of basis functions. Unlike a variational method, collocation determines basis function coefficients by demanding that the Schroedinger equation be satisfied at points: there are no integrals and no quadratures. In our calculations, collocation points are the points on a "sparse" grid. When using polynomial basis functions in a variational method, it is common to systematically reduce quadrature error by using more quadrature points than basis functions. Using more points than functions is unfortunately not straightforward in a MCTDH calculation. I shall discuss collocation methods that use more points than functions in order to systematically approach variational accuracy. To extract the best possible solutions from a given basis by using more points than basis functions means using rectangular matrices. Because the MCTDH basis is excellent, it is important to use rectangular collocation with MCTDH. This requires deriving new equations because the original MCTDH equations were derived with a variational approach. Excellent results are obtained for molecules with as many as six atoms without any need to optimize points.

Electronic coherences built by an attopulse control electron-nuclei entanglement and the forces on the nuclei

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Short attosecond (as) or few femtoseconds (fs) pulses have a broad enough energy bandwidth for exciting a superposition of several electronic states in neutral molecules and molecular cations. This opens the way to engineering electronic coherences to steer charge migration through the selective localization the electronic density on its purely electronic time scale.[1] As the nuclei begin to move, the electronic and nuclear motions are entangled and the engineered electronic coherences can be usefully exploited for control by steering the vibronic density through the network of non adiabatic interactions to specific products.

I will discuss several examples illustrating the role of initial entanglement and the features of the force on the nuclei exerted by the vibronic wave packet after excitation with an attopulse, first in the case of the fragmentation of diatomic molecules oriented with respect to the polarization of the exciting pulse.[2] I will then report on the force on the nuclei and the stereodynamics in an ensemble of initially randomly oriented molecules photoexcited by an ultrashort pulse: An ensemble of diatomic molecules LiH excited by a short CEP controlled IR pulse[3] and the forces driving the ultrafast structural rearrangement of the methane cation induced by photoionization of an ensemble of neutral CH_4 to a superposition of the three lowest states of the cation by a XUV pulse.[4]

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Vibrational, vibronic and electronic quantum dynamics with the MCTDH approach

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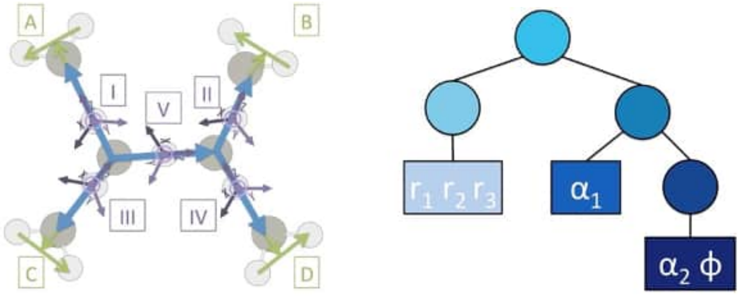
The multiconfiguration time-dependent Hartree (MCTDH) method and its multilayer (ML-MCTDH) generalization [1] constitute a powerful and general approach for the solution of the time-dependent Schrödinger equation for high-dimensional and highly correlated quantum mechanical systems. Here I will discuss some recent developments in our research group that have enabled applications to the spectroscopy and dynamics of complex quantum systems, both in the areas of vibrational and electronic quantum dynamics [2,3,4]. I close with some perspectives for further developments and standing challenges ahead.



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Multiscale Molecular Simulations of Microstructure of Ultraelastic Chemically Complex Metals

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High entropy alloys (HEAs) has attracted tremendous interests in both academia and industry because of their potential applications in advanced structural, energy, or catalytic materials. Recently a $Co_{25}Ni_{25}(HfTiZr)_{50}$ complex alloy with extraordinary elastic limit and Elinvar effects was reported [1]. Our extensive density functional theory (DFT) calculations indicate the local chemical ordering is the key to accommodate the 11% atomic size misfit. To further investigate the plastic behaviors of this complex ultraelastic alloy, we trained a machine learning (ML)-based energy model that can predict the energies and atomic forces with high fidelity to the DFT calculations, and performed a series of large-scale molecular simulations to examine the plastic deformation and dislocation dynamics[2]. Our simulations are in excellent agreements with experiments; furthermore, our simulations provide atomistic details of dislocation core structures, suggesting potential structural reorganization at elevated temperature, which are difficult to be extracted directly from experiments. Hence, we demonstrate that ML-based energy model is a powerful tool in studying the microstructure of chemically complex materials.

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Transfer Tensor Method and Applications to Cavity Polaritons

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The initial evolution of an open system encodes the essential information of its underlying dynamical correlations, which in turn predicts its trajectories at later times. In this talk, I will present a general strategy, Transfer Tensor Method (TTM), which stores the information from short-time trajectories in non-Markovian dynamical maps, compresses the maps into transfer tensors, and then uses the tensors to propagate the state of the system to longer time scales. As illustrative examples, TTM has been implemented to study quantum dissipation and relaxation of lossy cavity polaritons. As demonstrated in these examples, TTM is flexible to accommodate static disorder, kinetic analysis, basis reduction, and spatial-temporal correlation. In essence, TTM is a black-box tool, applicable to both quantum and classical systems, both discrete and continuous state variables, and both numerical and experimental data, and will find potentials in large-scale numerical simulations, machine learning, and quantum information processing.

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Fermi's Golden Rule Rates for Exciton Transfer and Nonradiative Decay Processes

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Great advances have been made during the past two decades in direct calculation of quantum transitions in complex molecular environments and intricate quantum dynamical processes. While full dynamics calculations may be ultimately necessary for satisfactory theoretical description of these transitions, it is often the case that transitions can be qualitatively characterized or semi-quantitatively modeled in terms of appropriate rates combined with master equations. For the calculation of rates, Fermi's golden rule (FGR) has been widely and successfully used for various molecular systems. However, in its applications to complex molecular systems, there are some ambiguities and issues requiring further refinement and development of FGR. This talk will provide a short summary of our FGR-based theories of resonance energy transfer and nonradiative decay processes that can account for new quantum effects that were missing in established theories. Applications of some of these to light harvesting complexes and organic dye molecules are demonstrated as well. We then provide our most recent theory of nonadiabatic transitions due to derivative couplings, which accounts for non-Condon effects and demonstrate the utility of the theory.

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Charge/energy transfer in organic aggregates simulated from stochastic Schrödinger equation

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Organic aggregate is one of novel materials with wide applications in the fields of photovoltaic and luminescence. Revealing the dynamic behavior of energy/charge transfer in these materials is significant to understand photoelectric performance and optimize organic optoelectronic devices. At the microscopic level, the dynamic processes of energy/charge transfer show both the characteristics of jumping motion with molecular localization and the law of wavelike motion in the energy band of inorganic semiconductor, which makes the rate theories and energy band theories inapplicable. To solve this problem, we have developed a rigorous stochastic Schrödinger equation and its approximation formula, in which the molecular vibration is introduced as a random fluctuation of the electron energy level, and thus the approach can be applicable to the dynamic process in the systems with nanometer scale. We also try to extend the stochastic Schrödinger equation to reveal carrier dynamics in oxide semiconductors in both the lattice momentum space and the coordinate space, and provide an innovation method in the field of inorganic semiconductor.

Doubly hybrid functionals: From molecules to extended materials

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Density functional theory (DFT) is now the most popular computational method in materials science. As the new generation functionals, doubly hybrid approximations (DHAs) have been shown to improve over conventional functionals with unprecedented accuracy in describing various kinds of chemical interactions and properties for finite molecules [1-3]. Recently, we have realized the periodic implementations of DHAs and demonstrated that the accuracy of DHAs achieved for finite molecules can be transferred to extended materials [4-7]. We anticipate that this new advancement will boost the predictive power for accurate descriptions of molecular crystals, as well as those of molecule-surface interactions in heterogeneous catalysis.

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Optical Spectra of periodic systems from *ab-initio* theories

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In the last two decades time-dependent density functional theory (TDDFT) has been increasingly applied to solids, and in particular to the calculation of optical spectra. In this talk I will first discuss how accurately this spectrum can be described within a pure Kohn-Sham time-dependent density-functional framework, i.e., a framework in which no theory beyond Kohn-Sham density-functional theory, such as GW, is required to correct the Kohn-Sham gap. Our approach relies on the link between the exchange-correlation kernel of TDDFT and the derivative discontinuity of ground-state DFT. I will show that semiconductors and wide-gap insulators are well described by our approach. Two-dimensional materials, instead, remain a challenge and better results are obtained using the Bethe-Salpeter equation of Many-Body Perturbation Theory. I will then point out the importance of being consistent between approximations employed in the ground-state calculations and approximations employed in the linear response calculations. I will illustrate this issue with the example of monolayer $NiBr_2$, for which a possible excitonic phase has been identified in the literature [3].

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Developing machine-learning-corrected density functionals free from error cancellation

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Machine learning (ML) has demonstrated its potential usefulness for enhancing the development of density functional theory methods. In this talk, I will present our recent efforts towards constructing ML models to correct density functional approximations (DFAs). Particularly, by using highly accurate total atomic and molecular energies as reference data for training, the resulting ML-corrected DFAs show substantially improvements over the parent DFAs for a variety of thermochemical and kinetic energies. This includes more accurate calculations of atomization energies, ionization potentials, electron affinities, bond dissociation energies, and barrier heights. Importantly, the ML-corrected functionals allow for fully self-consistent-field calculations with similar or even higher computational efficiency compared to the parent functional. This study highlights the promising potential of developing ML-corrected functionals that can perform uniformly better than current mainstream DFAs.

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Basis set error-corrected multireference random phase approximations for the correlation energy

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Recently we have shown that adiabatic connection (AC) formalism combined with particle-hole extended random phase approximation (phRPA) offers an appealing way for obtaining correlation energy for complete active space (CAS) reference wavefunction [1,2]. AC-phRPA requires only one- and two-electron reduced density matrices, admitting large active orbital spaces if combined with DMRG [3].

By establishing a formal connection between a second-order perturbation energy and AC correlation energy can be expressed through the particle-hole (ph), particle-particle (pp), or a combination of both (mixed ph-pp) channels. We will present applications of the ph, pp, and mixed ph-pp approaches, showing that the mixed ph-pp method offers good accuracy for both ground and excited multireference states.

In the second part of the talk, a basis set error corrected AC-phRPA variant will be introduced. The correction only requires modification of the AC Hamiltonian and comes at no extra cost.

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Multireference perturbation methods for exploring potential energy surfaces

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The geometry optimizations and molecular dynamics simulations are necessary to study dynamic procedures using quantum chemistry. Such applications greatly benefit from the availability of analytical nuclear gradients, *i.e.*, the first-order derivatives of electronic energy with respect to atomic positions.

This presentation discusses our recent developments in analytical gradient methods for the second-order multireference perturbation theories (PT2). With the PT2 analytical gradient theories, it is now routinely possible to conduct geometry optimizations and *ab initio* molecular dynamics simulations using the CASPT2, NEVPT2, (X)MCQDPT2, and SA-DSRG-MRPT2 methods.[1] If time is enough, we will also discuss our developments in the quantum chemistry methods using larger active spaces.

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Perturbation-adapted PT (PAPT): Analysis and Extension to the Multi-reference Level

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Many-body perturbation theory (MBPT) is routinely applied for describing correlation effects. Tuning low order MBPT corrections to improve accuracy without increasing computational cost, has been an ever present challenge. Choice of the zero-order problem, i.e. the partitioning provides ground for adjustments at the formal level. A partitioning optimization introduces parameters in the zero-order Hamiltonian and sets up equations for improving some property of the PT terms. The PAPT method of Knowles[1], is a partitioning optimization that seeks integrals of an effective one-body zero-order. Accuracy of PAPT in weak correlation scenarios is remarkable.

We present an analysis of PAPT both in formulae and in numerical terms. Relation with alternative strategies, in particular Davidson's *A*-matrix technique is pointed out.[2] The Hartree-Fock (HF) wavefunction based PAPT is broken down for level-shift and orbital rotation, allowing separate examination of individual components.[3]

Deteriorating performance of PAPT in situations affected by strong correlation is rooted in the HF determinant based formulation. To benefit of PAPT in such cases, a multi-reference (MR) version is devised, in the general framework of multi-configuration PT, developed in our laboratory.[4]

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Recent developments in multi-reference methods with large active space

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Multi-reference (MR) methods, including multi-configurational self-consistent field methods (MCSCF) and subsequent MR dynamic correlation methods, are widely used for the study of strongly correlated systems. In MR calculations, active spaces that include strongly correlated electrons and orbitals have to be defined. Based on iterative CI (iCI),[1] we developed a stable MCSCF method iCISCF, which is able to address systems with about one hundred active orbitals.[2] The iCISCF method has been further extended to include spin-orbit coupling (SOC) effects as well[3].

Based on MCSCF reference with large active space, such as iCISCF, the development of computationally efficient and robust post-MCSCF methods remains a challenge in quantum chemistry. Through the analysis of various approximations, we have identified a robust approach for the development of MRPT or MRCI methods using any MCSCF reference. [4,5] The new approach has been integrated into the ORCA and BDF packages.

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DFT reaction barriers: An adiabatic-connection perspective

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Reaction barriers in density-functional theory are considered from the perspective of the adiabatic connection (AC). A reaction AC integrand is introduced, which allows us to analyze the role of exchange and correlation contributions in determining reaction barriers [1]. Using Lieb maximization [2] the reaction AC integrand is computed to high accuracy and compared with those obtained via coordinate scaling from common exchange-correlation functionals [3].

This comparison clearly delineates the role of exchange and correlation in determining reaction barriers and error cancellations for common density functionals are revealed. Exchange contributions can be readily improved by inclusion of orbital-dependent exchange. However, the accurate treatment of the correlation contribution remains challenging, as reflected in the shape of the reaction AC and the behavior of approximate functionals under coordinate scaling. Implications for the design of density-functionals are considered.

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Toward Efficient and Unified Treatment of Static and Dynamic Correlations in Generalized Kohn–Sham Density Functional Theory

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Accurate description of the static correlation poses a persistent challenge in electronic structure theory, particularly when it has to be concurrently considered with the dynamic correlation[1,2]. In this talk, I will present a recent work in our group to develop here a method in the generalized Kohn−Sham density functional theory (DFT) framework, named R-xDH7-SCC15, which achieves an unprecedented accuracy in capturing the static correlation, while maintaining a good description of the dynamic correlation on par with the state-of-the-art DFT and wave function theory methods, all grounded in the same single-reference black-box methodology[3,4]. Central to R-xDH7-SCC15 is a general-purpose static correlation correction (SCC) model applied to the renormalized XYG3-type doubly hybrid method (R-xDH7). The SCC model development involves a hybrid machine learning strategy that integrates symbolic regression with nonlinear parameter optimization, aiming to achieve a balance between generalization capability, numerical accuracy, and interpretability. Extensive benchmark studies confirm the robustness and broad applicability of R-xDH7-SCC15 across a diverse array of main-group and transition metal involved chemical scenarios. Notably, it displays exceptional aptitude in accurately characterizing intricate reaction kinetics and dynamic processes in regions distant from equilibrium, where the influence of static correlation is most profound. Its capability to consistently and efficiently predict the whole energy profiles, activation barriers, and reaction pathways within a user-friendly “black-box” framework represents an important advance in the field of electronic structure theory.

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Hierarchically Correlated Orbital Functional Theory

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Kohn-Sham density functional theory (KS-DFT) and reduced density matrix functional theory (RDMFT) provide two distinct and precise theoretical frameworks for addressing many-electron problems. However, both approaches face challenges when dealing with static and dynamic correlation effects. In light of this, we have established the hierarchically correlated orbital functional theory (HCOFT) that unifies KS-DFT and RDMFT, creating new avenues to enhance the accuracy of electronic structure predictions. This report summarizes some of the work in my group in terms of foundational theories, calculation algorithms, and approximate functionals along this direction.

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FIREBALL2020: A Revitalized Paradigm for DFT Molecular Dynamics

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The development of DFT methodologies continues to mature as a useful tool for computational materials science. As "a rising tide lifts all boats", then so too do these advances in DFT contribute to advances in molecular dynamics capabilities with DFT used for direct evaluation of energies and forces. For machine learning algorithms, particularly time-series convolution methods, rapid, evolving acquisition of molecular-dynamics simulation data is imperative for training and validation [1]. We will discuss the latest developments of FIREBALL, an efficient, DFT molecular dynamics code using pseudo-atomic orbitals (numerical basis set) that does not require fitting of parameters [2]. FIREBALL2020 has greatly improved speed and numerical accuracy with implementations for ASE and with Multiwfn. FIREBALL is a very useful tool for generating data used in machine learning models that we have developed. The ability to calculate exactly the non-adiabatic molecular dynamics couplings in a local orbital basis has also enabled us to generate pertinent excited state potential energy surfaces and explore these with correct Hellmann-Feynman force representation [3].

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Universal and Updatable Artificial Intelligence-Enhanced Quantum Chemical Foundational Models

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I will talk about the paradigm change in computational chemistry we introduced: towards universal and updatable AI-enhanced quantum mechanical (UAIQM) models[1]. They are successors to the AIQM1 method[2] (~CCSD(T)/CBS accuracy at the semi-empirical cost). Models can also be combined to obtain accurate ensembles as we show for DFT.[3] Our methods are available in MLatom[4] and simulations can be run in the web browser at https://XACScloud.com.

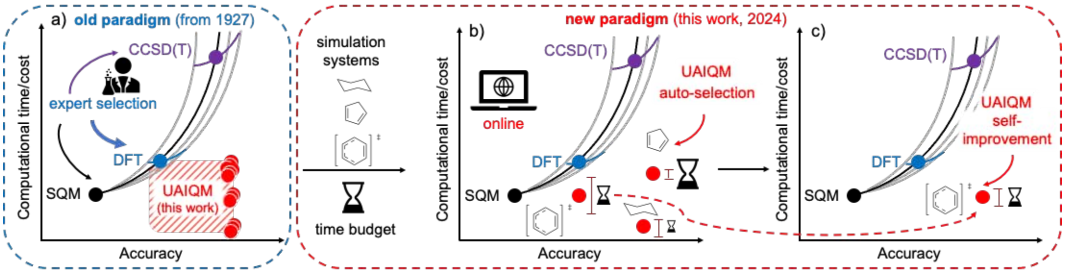

Figure 1. The introduced paradigm change in computational chemistry.[1]

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Deep Learning of Stability of Ligand-protected Gold Nanoclusters

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The stability or experimental accessibility of gold nanocluster, which is modulated by different ligands and doped metal atoms, is a prerequisite for the potential applications in energy materials, catalysis, sensors, bio-imaging, and therapy. For screening out the stable candidates from the complex combination space formed by different metal cores and ligands, it is crucial to predict the stability of the Au nanoclusters before the synthesis in experiment. A comprehensive dataset is established by determining the formation energies (E_{form}) of various Au nanocluster structures (including 21 different core sizes, 22 kinds of ligands, 7 kinds of doped metal atoms) using density functional theory (DFT) calculations. A deep learning model, graph convolutional neural network (GCNN), is applied to achieve good performance for formation energy predictions. The applicability of GCNN is further tested by using some external test sets, encompassing the synthesized nanoclusters of particular interest due to their responsiveness to stimuli and biocompatibility. The oil-water partition coefficient (logP) of ligand has great influence in the solubility of Au clusters and cell activity. The predictive deep learning model also guided the successful synthesis of some novel structures, e.g., $Au_{10}(PPh_3)_7Cl_3$ and $Au_{38}OT_{24}$ (OT = octane-1-thiol), with the predicted formation energies close to those known nanoclusters. The proposed machine learning scheme holds promise in facilitating the high-throughput discovery and synthesis of nanoclusters in experiment.

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Machine Learned Electronic Structures and Optical Properties for Organic Semiconductors

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Computational material discovery based on density functional theory (DFT) has achieved tremendous success in recent decades. However, the power of DFT on organic semiconductors (OSC) as molecular electronic materials suffer significantly from its computational complexity and intrinsic errors. Here we introduced a new exchange–correlation (XC) functional developed by us, referred to as ML-ωPBE, which evaluates the molecule-specific range-separation parameter (ω) in a range-separated hybrid (RSH) functional using a stacked ensemble machine learning algorithm and a composite molecular descriptor. [1] Compared to first-principles OT-ωPBE, a well-trained ML-ωPBE reaches a mean absolute error (MAE) of 0.00504 a_0^{-1} for optimal ω's, reduces the computational cost by 2.66 orders of magnitude, and achieves comparable predictive power in optical properties. In addition, ML-ωPBE shows a strong domain adaptation from closed shell molecules to open shell radicals. [2] From this study we concluded the importance of descriptors from semi-empirical quantum chemical calculations. Our study will set the stage for developing physics-based, and data-driven computational models for high-throughput material and drug discovery.

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Interfacial fluxionality in electrocatalysis: in and out of equilibrium

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Electrocatalytic interfaces under applied potential and in the presence of adsorbates dramatically reshape, as seen, for example, in *in situ* STM. I will present a theoretical framework to describe the dynamics of electrocatalytic interfaces, combining grand canonical DFT, global optimization under potential and adsorbate coverage, and the network of concurrent reaction pathways constituting the catalytic mechanism. Conditions radically reshape the interface, and change the accessible reaction mechanisms. To illustrate this, I will discuss size-selected supported Pt cluster electrocatalysts for HER. By combination of theory and experiment, we demonstrate that these clusters have exhibit strong fluxionality of structure and coverage as a function of voltage and the stage of the catalyzed reaction.[1,2] Metastable local minima are involved in the mechanism. The nature of the active sites strongly depends on the potential. This behavior inevitably leads to breaking scaling relations.[3] I will further show how fluxionality can actually be used as a tool in cluster electrocatalyst design.[4] Finally, the Cu cathode in the presence of CO and H or OH, characteristic of CO(2)RR, strongly restructures, and exhibits obvious off-equilibrium, kinetically-controlled reconstruction that we capture with frontier theoretical methods, and experiment.[5,6]

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Potential Dependence in Oxygen Evolution Reaction

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Oxygen evolution reaction (OER) is of crucial importance to sustainable energy and environmental engineering, and layered double hydroxides (LDHs) are among the most active catalysts for OER, but the reaction mechanisms remain controversial. Distinctive types of reaction mechanisms have been proposed for the O-O coupling in OER, yet they compose a coupled reaction network with competing kinetics dependent on applied potentials. We combine grand-canonical methods and micro-kinetic modeling to unravel that the dominant type of OER mechanism on LDHs is dependent on the applied potential.[1] Moreover, we identify the potential-dependent formation of fleeting active sites (FASs) on Ni LDH by Fe cations from the electrolyte and uncover a novel type of OER mechanisms thrust by FASs. We demonstrate that the fleeting-active-site-thrust (FAST) mechanism delivers superior OER activity via the FAST intramolecular oxygen coupling pathway. We further reveal that introducing only trace-level loadings of FASs on Ni LDH can significantly boost and govern the catalytic performance for OER.[2]

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Liquid metals as dynamic systems for atomically-precise control

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The manipulation of interatomic interactions for structural self-assembly is a seductive promise of nanotechnology, most tantalisingly made evident by biological examples in nature. Much of the promise of sustainability in materials science comes from the idea of such structural control being able to be achieved at low energetic cost.

At the risk of anthropomorphising atoms, this talk will present some examples of how, by developing an understanding of how particular atoms *want* to behave, we can manipulate structure by proxy. Not through forcible manipulation of atoms, but through understanding their environmental preferences, and how these change through changing many-body interactions as they assemble.

The use of low-temperature liquid metals, such as gallium, as media for the dilution of other metals has led to an increasing variety of examples of how temperature- and concentration-dependent interactions can be used to direct the self-assembly of nanostructure, with astonishing precision, resulting in novel pattern formation [1]. This talk will introduce the use of *ab initio* molecular dynamics for the elucidation of the mechanisms of structural formation, whether via the differential mobility of dopant metal atoms [2], or due to the formation of structure at the surface of the liquid metal [3], or indeed due to nanocrystal formation fully within the liquid metal environment [4].

It will also cover the use of such techniques to describe the differences between solid and liquid alloy catalysts, particularly relating to the dynamic behaviour of the surface as it interacts with reacting molecules [5,6]. Finally, it will finish with some comments on what these studies have taught us about the complex structure of the liquid environment itself.

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Integrative biochemical and simulation analysis of haloalkane dehalogenase mutants engineered by generative AI

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Haloalkane dehalogenases play a crucial role in the detoxification of biological media by accelerating the conversion of toxic haloalkanes into harmless alcohols. The enzymatic mechanism involves two chemical steps: an S_N2 nucleophilic attack (dehalogenation) and a subsequent hydrolysis step. We propose an advanced strategy to evaluate mutations of the haloalkane dehalogenase from *Xanthobacter autotrophicus* with improved catalytic power using generative AI predictions.

Generative AI leverages naturally evolved sequence information to uncover sequence-activity relationships in enzymes and has been effectively used to design functional enzymes. In this study, we employed a generative maximum-entropy model to design single and double mutants of the haloalkane dehalogenase. Our kinetic experiments, including stopped-flow analysis, identified mutants that enhance the catalytic activity of either the S_N2 step or the overall reaction, demonstrating the effectiveness of AI-driven enzyme engineering.

The experimental kinetic findings are supported by a theoretical analysis performed with the Empirical Valence Bond (EVB) method. Using EVB, we provide the structural, energetic, and electrostatic characteristics of the native dehalogenase and its designed mutants.

Landscape and flux theory of biological systems

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We developed a general landscape and flux theory for quantifying the driving force for the nonequilibrium biological system dynamics. We show that while the landscape drives the system dynamics down along its gradient, the flux is curl and tends to drive the rotational flow. Therefore, the global dynamics of the biological systems can be viewed as a charged particle moving under electric and magnetic field in the multidimensional state space. The dual driving forces of the landscape and the flux can have significant influences on the biological function and process characterized by the depths and widths of the basins of attraction, the barrier heights, the paths and the switching times of the state transitions. They also have the nonequilibrium thermodynamic counterparts such as the entropy production rate and heat dissipation. These global characterizations of the system can be used to identify the key elements and key regulations for the functions. Both low throughput real time experiments and high throughput sequencing experiments can now be utilized to quantify the landscape and flux. This provides a unique way by combining the theory and experiment together for understanding the underlying mechanisms of the biological important processes for the cell fate decision making and the oscillations such as the cell cycle and differentiation/reprogramming, as well as the more broad subjects in cancer, ageing, evolution and ecology [1,2].

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Nature's strategy for small molecule capture and reduction: Investigating chemistry in iron-containing enzymes using quantum mechanics/molecular mechanics (QM/MM) and broken symmetry

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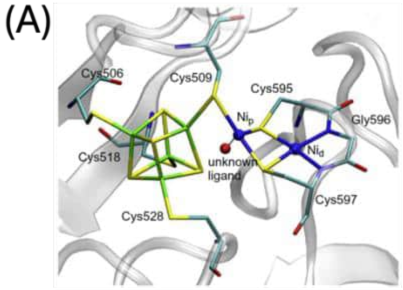
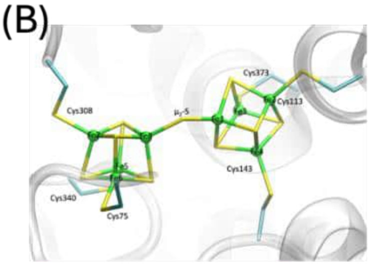
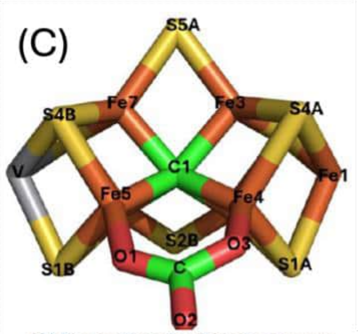
Nature's ability to capture and reduce small molecules, like N_2 or CO_2, requires energetic electrons and a catalyst. Here, we examine three metalloenyzmes that contain iron-sulfur cubane centers responsible for catalyzing reductive reactions: acetyl-CoA synthase (ACS) (Figure A), the double-cubane cluster protein (DCCP) (Figure B), and vanadium-nitrogenase (V-nitrogenase) (Figure C). Using hybrid quantum mechanics/molecular mechanics (QM/MM), we investigate structural and electronic properties of each of the enzymes, rationalizing a mechanism for substrate capture. In DCCP and V-nitrogenase, a broken symmetry approach is implemented to describe the multiple iron centers. Understanding these enzymatic mechanisms inspires synthetic enzymes capable of hydrocarbon formation under mild conditions.



(A) The active site of acetyl-CoA synthase (ACS). Figure taken from Elghobashi-Meinhardt et al. https://doi.org/10.1016/j.bbagen.2020.129579



(B) The active site of DCCP. Figure taken from Elghobashi-Meinhardt et al. https://doi.org/10.3390/catal11020245



(C) The active site of V-nitrogenase.

Towards Understanding the Mechanism of the Ultrafast Dynamics of Water Hydrogen Bonding Network in Bulk and Interfaces

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Hierarchical water motions on material surfaces in different conditions (temperature, hydration extent, pressure, etc.), as well as the coupling of this motion with the substrate/solute dynamics is a complex, long lasting, interdisciplinary research topic. We studied, theoretically, the molecular mechanisms of coupling between the picosecond dynamical onset of substrates and their surface water in the subzero temperatures. By combining with neutron experiments, we explored the dynamics of water and the underlying substrates independently below 0 °C across a broad range of materials. Surprisingly, whereas the function-related harmonic-to-anharmonic dynamical transitions in the materials exhibit diverse activation temperatures, the surface water presents a universal transition at a common temperature. Further simulations revealed that the universal transition of water results from an intrinsic surface-independent relaxation: switching of hydrogen bonds between neighboring water molecules with a common energy barrier ~ 30 kJ/mol. The iso-configurational ensemble analysis was applied to further study water motion at different local substrate environments, which connected the universal process observed to the water rattling motion within their confining cages, instead of the translational motion of water escaping the local cages. The reaction flow analysis revealed the correlation and causality among the water-water, water-protein hydrogen bond switching and protein surface atom rattling dynamics, which provides a picture about how the motion flows from hydration water into the substrate. The aforementioned energy barrier is passed on to the underlying substrates and drives the temperature dependence of the material-specific flexibility, crucial for the function of the materials below the freezing temperature.

Developing a molecular simulation package in connection with AI tools

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Abstract

Molecular dynamics simulation is becoming a powerful and useful tool for studies of complex molecular systems. In this talk, introduction will be given to a recently compiled molecular simulation package, SPONGE. In this package, we implemented a new electrostatics calculation method, which allows efficient computation of Coulombic interactions for various boundary conditions, including various periodic and equal potential boundary conditions. We illustrated the applications of these methods by studies of ion chain formation on metal surface. The simulation package is also equipped with various easy-to-use enhanced sampling methods, which allowed one to study chemical reactions and phase transition with high efficiency. In addition, a convenient interface is provided between MD simulation and quantum calculation software. The MD simulation program was also written directly on deep-learning platforms such as MindSpore and JAX, which allows us to take advantage of auto-differentiation and auto-parallelization to take the advantage of neural network force fields fitted directly from quantum chemistry calculations. We will also discuss other functions of this molecular simulation package. In particular, the modules for AI-based protein structure prediction as well as drug screening accelerated by GPU.

Keywords

MD simulation, software development, machine learning

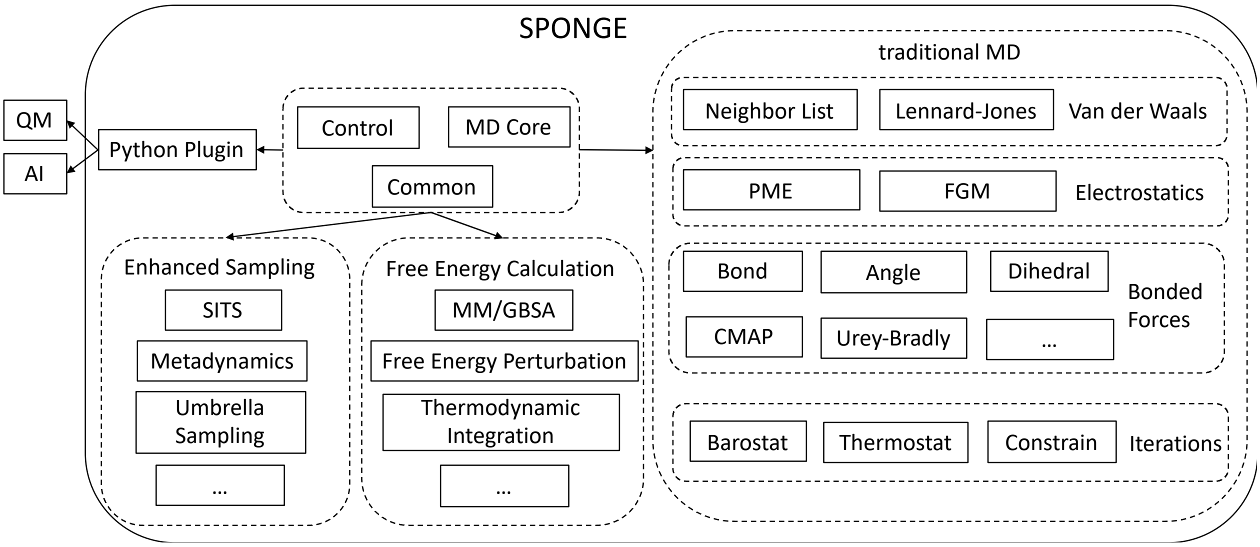

Figure: The overall framework of SPONGE

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Identification and Isomerization of Histidine Tautomers in Amyloid beta Peptides

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Recently, we suggested histidine tautomerism as another possible factor influencing misfolding and oligomerization during the pathogenesis of amyloidogenic diseases. Our lab demonstrated that these different protonated states in the histidine imidazole ring can be related to the conformational characteristics of diverse misfolded peptides (namely Amyloid beta (Aβ), tau, amylin, prion, etc.) by MD simulations.[1-3] His tautomers can provide a detailed microscopic understanding of the aggregation mechanisms which is difficult to be probed through experiments. We also compared β-sheet formation and histidine site-specific two-dimensional infrared (2D IR) spectroscopic signatures of Aβ dimers with different histidine states (δ; $N^{\delta1}$-H, ε; $N^{\varepsilon2}$-H, or π; both protonated) and the influence of metal nanomaterials.[4] The εεε:εεε dimer exhibited larger frequency shifts than δδδ:δδδ and πππ:πππ implying that the red-shift may have a correlation with $N^{\delta1}$-H (δ) protonation. In addition, for the first time, the effect of the static external electric field (EF) of varying intensities and directions on the conformational integrity and dynamics of two tautomeric isomers (εεε, δδδ) of β-Amyloid40 (Aβ) was studied.[5] In this context, we propose a useful technique to identify the histidine tautomers by X-ray absorption. We also, for the first time, observed the transition between histidine tautomers in real time MD simulations of Amyloid beta peptide with DFTB potential, and found the barrier is about 5 kcal/mol.

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MassCCS: Collision-Cross Section Calculations for Macromolecular Assemblies

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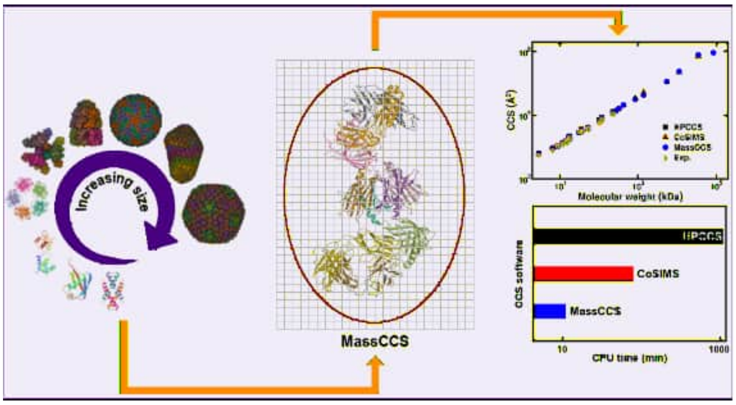
Ion Mobility Mass Spectrometry (IM-MS) is a highly accurate technique for the characterization of analytes and a valuable tool for the structural characterization of biomolecular systems [1]. The interpretation of IM-MS data is still a challenge and depends on accurate theoretical estimates of collision cross section (CCS) of the molecular target against the buffer gas. In this talk, I present MassCCS, a highly efficient and accurate new software for computing orientationally averaged CCS for ion-mobility mass-spectrometry ranging from small organic molecules to large macromolecular assemblies containing millions of atoms [2]. MassCCS combines the Trajectory Method and the linked-cell algorithm to achieve orders of magnitude speed-ups with respect to the fastest codes currently available for CCS calculations using the Trajectory Method.



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Exploring plant enzyme conformations and dynamics via MD simulations

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Molecular dynamics (MD) simulations have been widely adopted to complement experimental techniques in exploring the structures, dynamics and functions of biological macromolecules. In this talk, I will discuss my group's work employing MD simulations to probe the conformations and dynamics of several plant or fungal enzymes, including the hydroxycinnamoyltransferase (HCT), the aromatic amino acid decarboxylase (AAAD) and the isochorismoyl-glutamate pyruvoyl-glutamate lyase (IPGL). Common to these diverse systems is the critical role played by conformational dynamics, rather than static structural components alone, in mediating the unique function of each protein. I will highlight how their dynamics captured by MD have provided key insights into functions of these enzymes. Along this line, I will also briefly discuss our recent work on VacA, a bacterial pore-forming toxin, where conformational dynamics revealed by MD have been exploited to uncover its transmembrane channel structure and anion selectivity mechanism.

Transient delocalization in conjugated organic materials

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There is compelling evidence that charge carriers in organic semiconductors (OSs) self-localize in nano-scale space because of dynamic disorder. Yet, some OSs, in particular recently emerged high-mobility organic molecular crystals, feature reduced mobility at increasing temperature, a hallmark for delocalized band transport. Here we present the temperature-dependent mobility in two record-mobility OSs. By combining terahertz photoconductivity measurements with fully atomistic non-adiabatic molecular dynamics simulations, we show that while both crystals display a power-law decrease of the mobility (μ) with temperature (T, following: μ ∝ T^(-n)), the exponent n differs substantially. Modelling provides n values in good agreement with experiments and reveals that the differences in the falloff parameter between the two chemically closely related semiconductors can be traced to the energy-dependent delocalization of the states thermally accessed by the charge carriers, which in turn depends on the specific electronic band structure of the two systems.

A similar transient delocalization mechanism rules highly-efficient exciton diffusion in ordered OSs, showing great promise for facilitating long-range exciton transport, and charge transport at ultra-high doping concentrations. There, we find electrical conductivity to be strongly correlated with paracrystalline disorder rather than with Coulomb trapping. A general model for interacting electrons in highly doped polymers is proposed and carefully parameterized against atomistic calculations, enabling the calculation of electrical conductivity within the framework of transient localisation theory.

A unified picture for carrier transport in organic semiconductors

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Carrier transport in organic/polymeric materials has been a long scrutiny due to the complex interaction. We first demonstrated the importance of nuclear quantum effect for the carrier motion based on Fermi-Golden rule. We then applied the time-dependent matrix product state formalism to solve an electron-phonon coupling model with broad range of molecular parameters. We are able to provide a unified picture for describing the carrier transport in organic semiconductors, covering the hopping, phonon-assisted current, bandlike, and transient localization [1].

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Modelling intersystem crossing processes in thermally activated delayed fluorescence materials

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In this contribution I present computational protocols, to model excited state decay rate constants in thermally activated delayed fluorescence (TADF) molecular materials.[1] I first depart by presenting an extensive analysis of the models and parameters influencing the radiative rate[2] and the intersystem crossing (ISC) rate constants in aromatic molecules.[3] Further, protocols to predict TADF[4] in multiresonance (MR) TADF molecular systems are also presented.

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Computational Design of New Materials for Electronics, Energy and Environmental Applications

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Material properties are in-principle determined by electronic functionality. Now first-principles modelling can accurately calculate material electronic structure, allowing us to control electronic properties for illuminating "from the bottom up" structural, thermodynamics, and kinetic aspects of chemical and physical process, thus facilitating the rational design of new materials. In this presentation, we will choose some examples from our recent research showing how electronic functionality modulations via asymmetry, defect and ligand engineering to help the design (i) a novel 2D multiferroic dual transition-metal dichalcogenide for electronics application [1]; (ii) the optimal bimetal-doped $SrCoO_{3-\delta}$ perovskite as solid oxide fuel cell cathode [2]; (iii) a Cu-based metal–organic framework for the reduction of CO_2 into C2 products [3].

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Floquet non-adiabatic dynamics for strong light-matter interactions near metal surfaces

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light can modify chemical reactions and nonadiabatic electron transfer processes strenuously. In this talk, I will present our newly developed dynamical methods for treating strong light-matter interactions at metal surfaces. Such a scenario is very relevant to photoelectrochemistry, photo-catalysis, and plasmonic cavity. Two dynamical approaches—Floquet surface hopping and Floquet electronic friction—are developed to treat strong light-matter interactions near metal surfaces. We also formulate a Floquet Marcus nonadiabatic electron transfer rate. We find that the electron transfer rate shows a turnover as a function of the driving frequency of light.

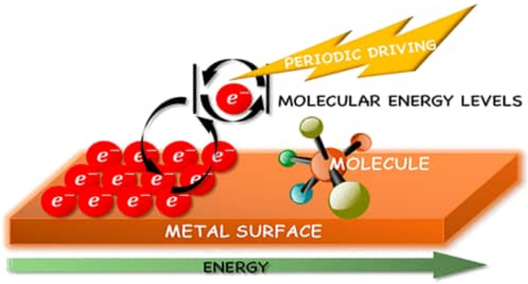

Figure 1. Nonadiabatic dynamics near metal surface subjected to strong light-matter interactions.

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Mixed Quantum-Classical Nonadiabatic Dynamics Methods and Applications to Large-Scale Semiconducting Materials

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Nonadiabatic dynamics in complex systems is one of the greatest challenges in theoretical chemistry. Although mixed quantum-classical dynamics methods have been widely utilized, it is still difficult to properly describe the complex quantum-classical correlation and the frequent surface crossings in large systems. Based on the principle of detailed internal consistency, we have developed a new theoretical framework for mixed quantum-classical dynamics and obtained reliable results by the wave function [1-4]. In addition, we have proposed large-scale nonadiabatic dynamics methods without explicitly using the nonadiabatic couplings and successfully studied graphene nanoribbons, transitional metal dichalcogenides and quantum dots with even tens of thousands of atoms using machine learning Hamiltonians [5-6].

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Crystal embedded multi-reference study of strongly correlated materials

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Modelling electronic and optical properties of materials containing transition metal (TM) atoms with isolated, highly correlated *d*-shells, either as a part of their crystal structure or as point defects, represents an ongoing challenge to the state-of-the-art computational methods. We have developed a rigorous crystal embedded multi-reference method of electronic structure calculation, named the periodic Effective Hamiltonian of Crystal Field (EHCF) [1], suitable for accurate description of strongly correlated *d*-shells in periodic systems.

For a variety of solid-state materials and with modest requirements for computational resources, EHCF accurately reproduces the experimental energy of *d*–*d* transitions and spin symmetry of both ground and excited states. Our initial test materials included metal oxides, carbodiimides, hydrocyanamides, and metal-organic frameworks, [1,2] including those displaying spin crossover behaviour demonstrated by a change in the spin state of a TM ion triggered by external stimulus. [3]

EHCF also shows a superior performance over the multi-reference complete active space self-consistent field (CASSCF) and single-reference density functional theory (DFT) methods for predicting the complex electronic structure of chromium (III) dopants in α-Al_2O_3, AlB_4O_6N and $BeAl_2O_4$ oxide materials. [4] An additional unique feature of the method is the ability to calculate the quadrupole splitting in ^{57}Fe Mössbauer spectroscopy, frequently used in experimental investigations.

In the future, we aim to embed the periodic EHCF [1] as the method of choice in materials design for quantum technologies, low-dimensional quantum materials, and two-dimensional semiconductors.

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Visible-light-driven Overall Water Splitting with Covalent Organic Frameworks

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Using solar energy to split water into hydrogen and oxygen is a crucial method for obtaining clean hydrogen energy and addressing energy and environmental challenges. Recently, organic polymers have emerged as promising materials for photocatalytic water decomposition due to their tunable optical and electronic structures at the molecular level. Designing the energy band structure of organic polymers to achieve efficient water photolysis under visible light is a key challenge in this field. We utilized first-principles electronic structure calculations to effectively regulate the valence and conduction band structures of two-dimensional organic polymers. By selecting specific molecular types for connecting groups and nodes, we identified carbon-nitrogen-based two-dimensional conjugated porous polymers suitable for visible-light catalysis and oxygen production. Our theoretical predictions align with experimental studies. Additionally, we predicted a series of 2D organic polymer photocatalytic materials capable of complete water decomposition by screening a database of 2D organic polymers. Finally, we developed a strategy to design these materials using functional molecular motifs to achieve overall water splitting under visible light irradiation.

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Relativistic couple cluster investigations of atomic properties of the heavies elements.

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Theory can provide important support at all the stages of spectroscopic experiments, from planning the measurements, through extracting the properties of interest from the data, and to the interpretation of the results and their comparison to theoretically predicted values. To this end, highly accurate calculations of atomic properties are needed. In order to be reliable, such calculations must include both relativistic effects and electron correlation on the highest possible level.

Relativistic coupled cluster is considered one of the most powerful methods for accurate calculations of properties of heavy many-electron systems. This approach can be used to obtain ionization potentials, electron affinities, excitation energies, hyperfine structure parameters, and other atomic properties, and a variety of molecular properties. It has been shown to be extremely reliable and to have very strong predictive power. Recently, we have developed a scheme that allows us to use extensive computational investigations to assign uncertainties on the theoretical predictions [1], facilitating the use of these predictions in experimental context.

A brief introduction to the relativistic coupled cluster method will be provided and the new development for estimation of uncertainties will be presented. The talk will focus on recent successful applications of the coupled cluster approach to atomic properties, focusing on the heaviest elements [2-4].

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Bound-state relativistic quantum electrodynamics: a perspective for precision physics with atoms and molecules

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Precision physics aims to use atoms and molecules to test and develop the fundamental theory of matter, possibly beyond the Standard Model. Most of the atomic and molecular phenomena are described by the QED (quantum electrodynamics) sector of the Standard Model. Do we have the computational tools, algorithms, and practical equations for the most possible complete computation of atoms and molecules within the QED sector? What is the fundamental equation to start with? Is it still Schrödinger’s wave equation for molecular matter, or is there anything beyond that? In my talk, I will review recent progress with the equal-time Bethe-Salpeter equation [1,2], the no-pair Dirac-Coulomb(-Breit) approximation, its high-precision numerical solution [3], and connections to non-relativistic QED as well as relativistic quantum chemistry. Ongoing work and future prospects for the precise computation of the pair-, retardation-, and radiative corrections to the correlated relativistic energy [4] are outlined.

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Role of spin-orbit effects in the relationship between NMR shielding and nuclear spin-rotation tensors

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A procedure to obtain experimental absolute scales of NMR shieldings was proposed more than fifty years ago by Ramsey and Flygare [1,2]. Although they established a very precise relationship between shielding and nuclear spin-rotation (NSR) constants, it was shown that their model is not applicable to molecules containing heavy elements. This fact motivated the development of new NSR tensor theories that include electronic relativistic effects. Based on one of these theories [3], we proposed a relativistic model that generalizes Flygare's relation [4]. In this talk, I will discuss the crucial role that spin-orbit effects play in the generalized relationship between the two molecular properties, also showing that these effects are equally essential in linking their parity-violation contributions [5,6].

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A variational reformulation of molecular properties in electronic-structure theory

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

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In silico spectroscopy
on classic and hybrid quantum computers

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Spectroscopy, the most far-reaching analysis tool in chemistry, exploits the interaction of light with matter to probe molecular and electronic structures. This interaction is also the foundation of photochemistry, optogenetics, phototherapy, photocatalysis, optical devices, solar cells, and other use cases in chemistry, life sciences, and material design.The theoretical modelling and simulation of the molecular response to light thus provides crucial fundamental understanding of the microscopic mechanisms behind all spectroscopies and light-energy conversion processes.

In my talk, I will present some recent results of our research efforts concerning: (1) theoretical X-ray spectroscopy to unravel ultrafast relaxation pathways in functional molecules [1-3]; (2) the development of response algorithms for hybrid noisy intermediate-scale quantum (NISQ) computers [4-6].

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Reduced-Scaling Coupled Cluster Theory in the Frequency and Time Domains

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The successes of reduced-scaling coupled-cluster approaches are well known for reaction energies, thermodynamic constants, dipole moments, etc. — properties that depend primarily on the quality of the ground-state wave function. However, much more challenging are higher- order properties such as polarizabilities, optical rotations, and others that also require accurate representation of the response of the wave function with respect to external electromagnetic fields. This lecture will provide an overview of our recent efforts to improve the description of such perturbed wave functions, from the development of field-aware densities to streamline local pair-natural orbital methods for frequency-dependent response theory to the use of local correlation techniques to reduce the cost of time-dependent coupled-cluster simulations of absorption and circular dichroism spectra.

Relativistic Real-Time Time-Dependent Density Functional Theory for Valence and Core Attosecond Pump-Probe Spectroscopic Processes

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First principles theoretical modeling of out-of-equilibrium processes observed in attosecond pump−probe spectroscopies triggering pure electron dynamics remains a challenging task, especially for heavy elements and/or core excitations containing fingerprints of scalar and spin−orbit relativistic effects. To address this, we introduce a methodology for simulating pump−probe spectroscopies within the relativistic real-time, time-dependent density functional theory (RT-TDDFT) framework, for both the valence and core energy regimes [1]. In addition to the full four-component (4c) Hamiltonian, we also introduce the atomic mean-field exact two-component (amfX2C) Hamiltonian accounting for one- and two- electron picture-change corrections within RT-TDDFT [1-3]. amfX2C preserves the accuracy of the parent 4c method at a fraction of its computational cost [3,4]. Finally, we apply the methodology to study valence and near-$L_{2,3}$-edge pump−probe spectroscopic processes of experimentally relevant systems and provide additional physical insights using relativistic nonequilibrium response theory [1,5].

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Towards Systematic Many-Body Treatment of Excited-State Phenomena in Solids

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Quantitative first-principles description of excited-state properties in bulk solids and solid-state defects remains a fundamental challenge in computational chemistry and physics. In this talk, I will describe several recent developments of an ab initio Green's function embedding framework for capturing local and non-local electron correlations in solids. I will first present a systematic study of spectral properties of strongly correlated open-shell transition metal impurity states in bulk copper, known as the Kondo problem, by combining ab initio dynamical mean-field theory, active-space density matrix renormalization group, and periodic quantum chemistry approaches. We demonstrate the possibility towards an exact quantum many-body treatment of the Kondo effect by comparing against experimental measurements. I will then present a new Green's function embedding formalism with interacting and correlated bath, which shows promise in capturing long-range electron interactions in semiconductors and metals at the coupled-cluster level.

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Modelling photoinduced charge transfer with polarizable embedding

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Photoinduced charge-transfer (PCT) underlies numerous processes in e.g. organic photovoltaics, photoredox catalysis, and photosynthesis; however, the optically dark and transient nature of PCT states complicates their experimental detection and motivates theory. Multiscale methods such as quantum mechanics/molecular mechanics (QM/MM) are popular, wherein the system is partitioned into an active QM region containing the molecules of interest which are embedded in an environment that is described with computationally cheap MM forcefields. However, an accurate treatment of CT states requires inclusion of electronic polarization of the environment, e.g. with polarizable embedding. Questions then arise on how to treat electronic states in a consistent manner when they cross during a reaction, i.e. at conical intersections (CI).

Building on an old idea from Thole, we developed an approach called integral-exact direct reaction field (IEDRF) that successfully describes CIs.[1] The embedding potential contains zero, one, and two-electron contributions that correctly screen Coulomb interactions and stabilize CT states. The method was implemented for graphical processing units at many electronic structure levels, including CIS, TDDFT, CASCI, and CASSCF, as well as their analytical gradients.

We benchmarked IEDRF on a series of solvated donor-acceptor dyes and found quantitative agreement (0.03 eV) with full-system results. Next, we explored the photosynthetic purple bacteria reaction center (PBRC) and found that electronic polarization both stabilizes CT states by ~1 eV and leads to asymmetry between the two branches of pigments. Our results support a view that unidirectional charge separation in PBRC arises from different effective dielectric constants in its active and inactive branches.

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Dynamics Chemistry for the Excited Systems: A Combined *Ab Initio* Molecular dynamics and Machine-Learning Simulation Strategy

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Accurate *ab initio* molecular dynamics (AIMD) simulation of the excited state systems is still a challenging topic in the fields. In this report, we share our recent progresses on the singlet fission systems and solvated electron systems as the followings.

(1) Singlet fission systems: The main points include the ergodicity-based AIMD simulation, singlet pre-fission energetics and AIMD-based statistics prediction of singlet fission mechanisms, dynamic cooperation effect of neighboring monomers in the excited state functional processes, and development and application of AIMD-based machine-learning method in exploring the structures and properties of the excited state functional processes, etc.

(2) Solvated electron systems: we present a series of investigation on the structures, reactivity and relevant dynamics of solvated electron systems using the AIMD simulation technique and AIMD-based machine-learning simulation strategy.

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Energy decomposition analysis method for qualitative and quantitative interpretations

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Intermolecular interactions in complex systems are important but challenging due to the large number of interacting molecules and the complexity of environments. In this talk, firstly, a density matrix strategy-based EDA method for many-body intermolecular interactions, called DM-EDA[1], will be introduced. Different from traditional EDA methods, instead of intermediate state wave function, the EDA terms in DM-EDA are expressed in the forms of density matrix. The density matrix based framework and the batch wise algorithm ensure that DM-EDA can be used for interactions involving a large number of monomers efficiently. Second, an extension of DM-EDA, called DM-EDA(RS),[2] will be presented. In DM-EDA(RS), the EDA terms are expressed as the summations of grid-based energy density in real-space. A certain kind of interaction term is not only a single number, but also the atomic contributions in the supermolecule or grid contributions in the whole space that can be visualized with 2D or 3D pictures. It provides not only the comprehensive explanations for intermolecular interactions, but also the insights for sub-region interactions involving different functional groups.

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AI4Green: An open source ELN for green and sustainable chemistry

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Digital tools will be a critical part of making chemistry research laboratories more sustainable. The AI4Green open-source electronic laboratory notebook (ELN), https://ai4green.app, combines features including data archival and collaboration tools [1]. It is a web-based application and free to use. As users plan their chemical reactions and record them in the ELN, green and sustainable chemistry is encouraged by calculating green metrics and colour-coding hazards, solvents, and reaction conditions. A Summary Table is automatically generated by AI4Green, showing Red-Amber-Green colour-coded sustainability metrics from CHEM21 and other considerations related to the Design Principles of Green Chemistry. The application's design facilitates the development and integration of auxiliary sustainability applications. For example, the open-source retrosynthesis software, AiZynthFinder from AstraZeneca has been integrated into the platform, providing an AI-powered guidance on synthesis routes to molecules. AI4Green features a user-friendly sustainable solvent selection tool, which comprises the Solvent Guide [2] and the Solvent Surfer. The latter is an interactive principal component analysis (PCA). This provides a simple intuitive interface that provides users with a quick and easy method to determine greener solvent alternatives and allows the exploitation of interactive PCA to tailor embeddings to their specific purpose.

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Data-driven Materials Science for Energy Sustainability

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Data-driven materials discovery is coming of age, given the rise of 'big data' and machine-learning (ML) methods. However, the most sophisticated ML methods need a lot of data to train them. Such data may be custom materials databases that comprise chemical names and their cognate properties for a given functional application; or data may comprise a large corpus of text to train a language model. This talk showcases our home-grown open-source software tools that have been developed to auto-generate custom materials databases for a given application.[1-4] The presentation will also demonstrate how domain-specific language models can now be used as interactive engines for data-driven materials science.[5-6] The talk illustrates the application of these data-science methods using case studies from the energy sector. The talk concludes with a forecast of how this 'paradigm shift' away from the use of static databases will likely evolve materials science.

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Quantum Alchemy: Treating Chemical Space with perturbations

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Estimating properties for large search spaces is a common problem. While quantum chemistry methods allow computation of many fundamental properties, this is a costly approach. While machine learning approaches interpolate between such data, quantum alchemy allows for extrapolation. As a perturbative approach, many diverse properties such as energies, orbital eigenvalues, electron densities, photoelectron circular dichroism parameters and protonation energies can be predicted with the simple closed form expression of quantum alchemy. At heart, a Taylor approximation is built from the first low-order response functions of the property w.r.t. changes in the nuclear charges and geometry. End-to-end, this is typically five orders of magnitude cheaper than quantum chemistry methods of comparable accuracy, which will further improve with differentiable quantum chemistry calculations. Constraining models by inclusion of this gradient information may prove beneficial.

Moreover, the closed-form expression of quantum alchemy models can be analysed particularly well. For energies, we obtain approximate symmetries which must hold true for all conceivable systems of certain structural properties, which can help machine learning models by reducing the search space. We also show that this allows to estimate the intrinsic dimensionality of a chemical property which in turn allows to estimate the best achievable data efficiency in models.

Atomly.net: Paving a data-centric high-way for materials science

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In this talk, the speaker will present how he takes all the technologies that have disrupted other industries and start to disrupt his own. By utilizing recent advancements in high-throughput first-principles calculations and AI, his team has developed a premier materials database, atomly.net, which provides scientists worldwide with access to a trove of high-quality materials science data. This comprehensive database includes first-principles calculation results for over 300,000 inorganic materials and a range of related properties, such as crystal structure, electronic structure, elasticity, and dielectric tensor.

With this extensive data resource, it becomes possible to efficiently screen, predict, and discover new materials in a cost-effective manner. This includes identifying potential quantum materials [1], screening feasible energy materials [2], extracting insights and trends from transition metal oxides [3], and creating generic artificial intelligence models for property predictions [4].

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Success of Treating Topological Dynamic Propagation in Polymer System with 1D Ising Model: A Novel Full-Scale Dynamics-Preserved Coarse-Grained Polymer Model

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Coarse-grained (CG) MD model for polymer system often has large deviation in dynamics from reference all-atomistic (AA) model [1]. For polymer systems, although Mori-Zwanzig theory has revealed the existence of complex space-time dissipations arising from inter- and intramolecular interaction competitions [2,3], it remains practically a formidable task to construct a dynamics-preserved CG model [4]. In this work, we found that 1D Ising model can be used to describe the intramolecular topological propagation. Based on this, we developed a parameter-optimization free CG model which can preserve dynamics across all-scales, ranging from local monomeric collisions at short-time scale to free diffusions at long time-scales.

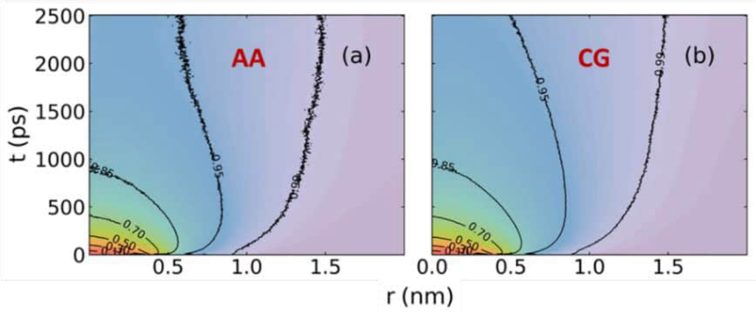

Figure 1. Van Hove functions calculated from (a) AA and (b) CG simulations.

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The QuantVec Software Suite for Next-Generation QTAIM

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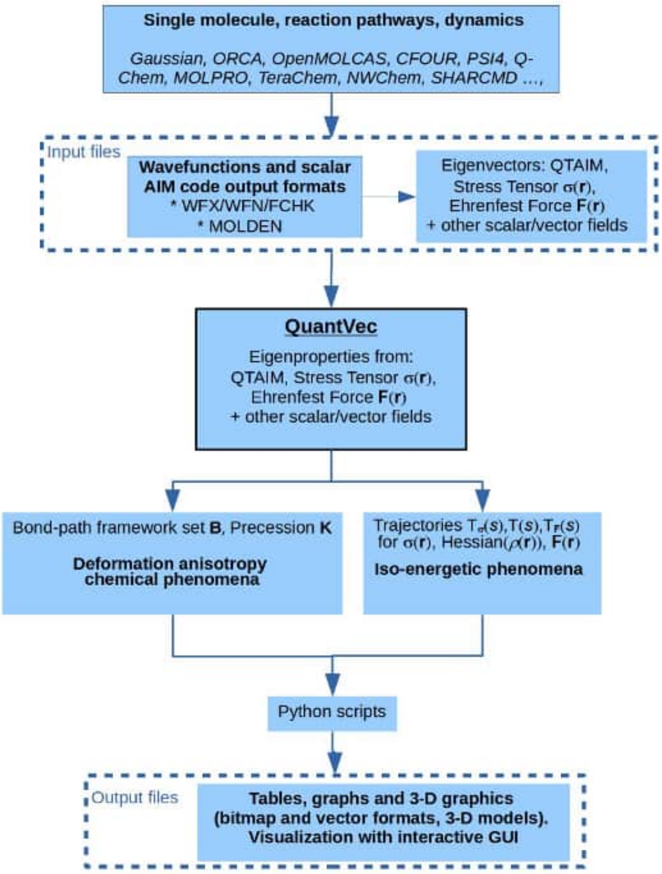
The QuantVec program package[1], takes either input wavefunctions from first-order density matrices expressed in an MO basis using Gaussian-type primitives in the WFX/WFN file format, or gridded charge density distributions in Gaussian `.cube` format produced by a very wide range of electronic structure codes. Widely-used MOLDEN-format files can be converted to WFX/WFN using the open-source Molden2AIM code [2]. Gridded density data is processed using the open-source CRITIC2 code[3]. The QTAIM, stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ and Ehrenfest force $\mathbf{F}(\mathbf{r})$ partitioning eigenvector-derived properties are then extracted using QuantVec[4,5]. Progress on the development of the software suite, including visualization capabilities, is outlined and illustrated with examples.



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New opportunities of photophysics and photochemistry studies using the BDF program

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The computational study of excited state processes is pivotal for the design of novel optoelectronic materials, light-sensitive materials and photocatalysts, among others. For a long time, a large portion of computational studies of excited states are limited to vertical absorption (e.g. UV-Vis) and emission (fluorescence and phosphorescence) calculations, due to a lack of efficient and accurate algorithms and programs for studying the dynamical properties of excited states, e.g. the rates of internal conversion (IC), intersystem crossing (ISC), electron transfer and energy transfer processes.

The BDF (Beijing Density Functional) program, which was an in-house academic code before 2022 and commercialized thereafter, was developed by a team of mostly Chinese quantum chemists, and is known for its highly accurate relativistic methods (Q4C, X2C), fragmentation methods (FLMO, iOI), as well as various excited state methods[1]. Highlights of the BDF program include: (1) the first implementation of TDDFT nonadiabatic coupling matrix elements (NACMEs) between two excited states, enabling the quantitative computation of excited state-excited state IC rates of large systems; (2) the first implementation of spin-orbit coupling (SOC) matrix elements at the sf-X2C-TDDFT level, making the accurate calculation of ISC rates of heavy atom-containing molecules possible; (3) the first rigorous spin-adapted TDDFT method (X-TDDFT) as well as its analytic gradient, which provides access to spin-adapted excited states of open-shell molecules; (4) a family of multireference configuration interaction (MRCI) and perturbation theory (MRPT) methods based on the static-dynamic-static (SDS) formalism, which achieves uniform accuracy for systems with densely spaced electronic states; and (5) energy- and electron-transfer integrals, which allow the evaluation of the rates of excited state energy and electron transfer processes.

The present report will briefly introduce these special features of BDF, followed by three application examples: (1) the inhibition effect of atmospheric soot particles on the photolysis of the pesticide imidacloprid; (2) the Rh-C bond photolysis mechanism of porphyrin rhodium(III) alkyl and acyl complexes [2]; and (3) the thermally activated delayed fluorescence (TADF) and phosphorescence of open-shell porphyrin copper(II) complexes [3].

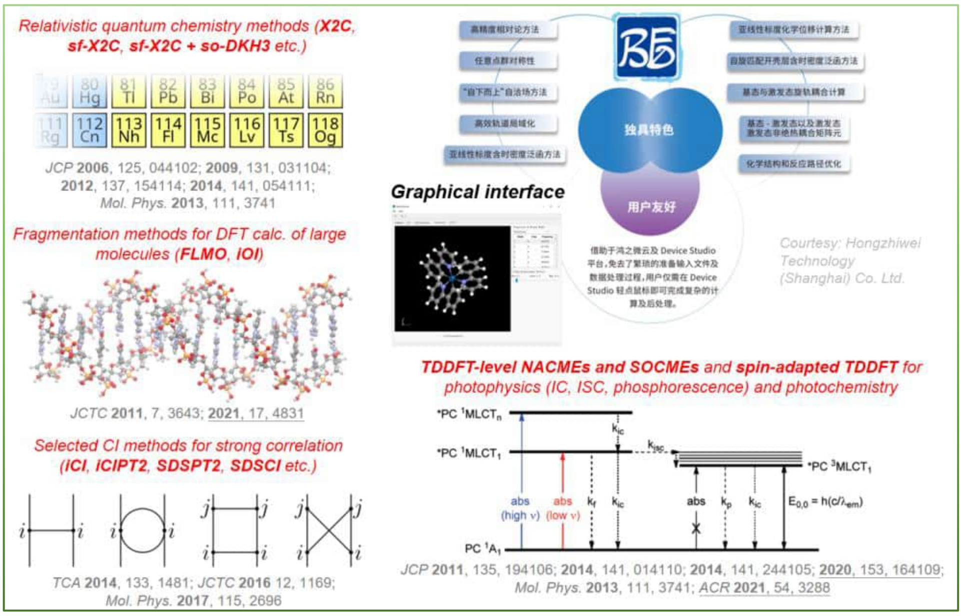

Figure 1. Selected feature highlights of the BDF program.

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MOKIT: an open-source package that combines the strengths of existing quantum chemistry software

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MOKIT (https://gitlab.com/jxzou/mokit) is an open-source package which offers various utilities to transfer molecular orbitals (MOs) among a dozen of quantum chemistry software packages. By utilizing the utilities, one can obtain the same SCF solution in different software without any effort for complicated open-shell species, perform various accelerated energy decomposition analysis (EDA), and convert wave function files back and forth. Moreover, MOKIT has intelligent built-in workflows for automatic as well as black-box multi-reference computations. The user need only write a Gaussian-syntax input file and then the RHF/UHF calculation, wave function stability check, orbital localization, orbital paring, GVB, CASSCF, etc. will be performed sequentially. The active orbitals as well as active electrons are determined automatically during computations and no human intervention is required. One can specify a preferred CASSCF package like PySCF, ORCA, Molpro, or PSI4 with a simple keyword, thus saving a lot of time to learn the usages and syntax of multiple software packages. The output of such a workflow has the same format of energies, properties and final orbitals printed no matter which programs are called. Advantages of existing quantum chemistry software are integrated together to perform highly-efficient computations. Embedding, multi-level or fragmentation methods combining different theoretical methods can also be developed easily based on MOKIT.

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AI acceleration of AIMD simulation of dynamic catalysis

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Elucidating the nature of active sites in catalysis and the mechanism how the special arrangements of atoms can facilitate chemical reactions, has always been one of the holy grails that generations of chemists have dreamed of. Combination of advanced experimental techniques and computational methods makes it possible to characterize the structures of active sites and unravel the reaction mechanisms at a molecular level. Challenges still remain when attempting to study catalysis at experimental conditions and during reaction turnover, and indeed many recent research efforts focus on in situ probing dynamical changes in catalyst structures. So far, the majority of studies still take a rather ‘static’ view of active sites and neglect the coupling of structural dynamics of catalysts with elementary reactions. This is mostly justifiable because from the viewpoint of elementary reactions occurring at the timescale of picoseconds, the catalytic sites are essentially static considering the catalyst structures usually evolve at macroscopic timescales. The fundamental question yet to address is what if the timescale of structural dynamics of catalysts overlaps with that of elementary reactions.

In this talk, I will show our ab initio molecular dynamics (AIMD) calculation predicts solid-to-liquid phase transitions of the metal clusters induced by the change of reaction species along the reaction coordinate, providing strong evidence that catalyst dynamics can play a crucial role in chemical reactions. Our finding therefore adds a new perspective on understanding of heterogeneous catalysis. Note also that the theoretical approach we use, including ab initio molecular dynamics and free energy calculation, is fundamentally sound, and makes no assumption that would affect our conclusions. Then, I will also present our latest development on AI accelerated AIMD (AI^{2}MD) calculation of dynamic catalysis at much larger space and time scale, showing great promise for in situ modeling of realistic catalytic systems.

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Short Bio (100-150 words)

Jun Cheng received his PhD in theoretical chemistry from the Queen’s University Belfast in 2008. He spent five years at University of Cambridge as a postdoc in theory sector in chemistry, and a junior research fellow at Emmanuel College. He is currently a Professor at College of Chemistry and Chemical Engineering, Xiamen University. His research interests are computational electrochemistry and theoretical catalysis. In particular, his group focuses on developing computational methods combining electronic structure theory, machine learning potential and molecular dynamics to simulate electrochemical interfaces and catalyst dynamics. He is an Associate Editor of The Journal of Chemical Physics, and has received the Alexander Kuznetsov Prize for Theoretical Electrochemistry of the International Society of Electrochemistry.

Cluster embedding and a grand-canonical hybrid explicit/implicit solvation model for computational catalysis

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In this talk, I will present our current developments on embedded cluster models for metallic systems. I will show what motivates us to simulate surface reactivity with cluster models and present a method for a consistent active space selection in projection-based DFT-in-DFT embedding along predefined reaction coordinates.[1]

I will then present a novel microsolvation model that allows for explicit sampling of a small region around a given solute in a grand-canonical scheme.[2] Key to this model is a probabilistic interpretation of the thermodynamic variables in the small explicit subsystem. While several models[3] exist that incorporate spatially resolved information on the solvent distribution in the implicit description, they rely on *ad hoc* closure equations that strongly affect the results of a simulation. In contrast, our approach gathers the relevant information from explicit grand-canonical sampling. While our approach is computationally more demanding than implicit solvation models, it is much more economical than fully explicit calculations. With accurate neural network potentials[4] emerging as surrogate models with *ab initio* quality, we expect our systematically improvable model to be a strong competitor to highly parameterized state-of-the-art solvation models.

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A Theoretical Perspective of Spin control on Iron-catalyzed reactions

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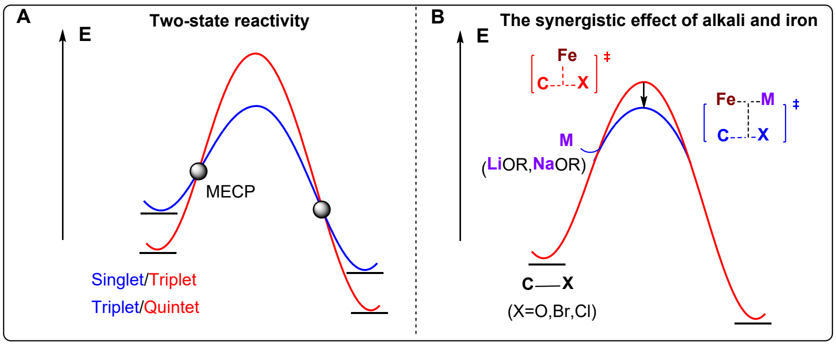
The low crystal field splitting energy of iron leads to its variable valence and spin states in actual catalytic conversion reactions, bringing new opportunities for reactivity regulation and challenges to understand reaction mechanism. Here, We reported the electronic structures of different spin states of a series of iron organic complexes and their catalytic reaction mechanisms. By studying the activation of iron catalyzed nitrogen gas, the hydrosilylation of olefins, the stepwise defluorosilication of bifluoroalkenes, and the ring opening silicification of benzofuran[1]-[4], the spin polarization effect and two state reactivity were proposed to follow the 9-orbital rule for open shell system with single occupied electrons (Figure 1. A). Our study also revealed that the synergistic effect of alkali and iron are important for achieving efficient catalytic conversion. A high spin iron catalytic cycle was proposed and the activation mechanism of alkali cations assisting low valent iron to jointly achieve C-X bonds was revealed in the cross-electrophile coupling reaction[5],[6] (Figure 1. B).



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We are working on the mechanism of selectivity regulation in organic reactions, focusing on the flexible conformation of molecules and electron spin interaction, revealing the interesting mechanism of asymmetric chemistry and iron/rare-earth metal chemistry, and improving the chemical understanding. We have published more than 50 SCI papers as (co-)corresponding authors, including *Acc. Chem. Res.*, *Chem*, *Nature. Commun.*, *J. Am. Chem. Soc.*, etc. I was awarded the second prize of the National Natural Science Award 2013 (5th), the EU Marie Curie Fellowship (IIF) (2015), the National Talent Program(2017), the Tianjin Outstanding Youth Fund (2019), and the Thieme Chemistry Journals Award (2020). I was appointed as a young editorial board member of China Chemical Letters (CCL) in 2022, awarded as a highly cited scientist by Clarivate Analytics in 2022 and 2023, and elected as a member of the Committee on Computational Chemistry of the Chinese Chemical Society.

Efficient simulation of photo-induced dynamics processes and their spectroscopic characterization

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Modern techniques of ultrafast laser spectroscopy and ultrafast X-ray (electron diffraction), which are capable to achieve femtosecond and even attosecond time resolution and high spatial resolution, provide excellent probes of chemical reactions in various molecular systems. The constantly increasing body of experimental data on molecular and chemical reaction mechanisms necessitates the development of accurate theoretical methods, which enable us to explain spectroscopic signals of molecular systems as well as their associated structural changes in terms of the underlying nuclear and electronic dynamics. In the past years, I have developed various numerical methods based on variational wave function, quantum master equation, stochastic Schrödinger equation, mixed quantum-classical methods as well as machine learning techniques for the efficient simulation of quantum dynamics and nonlinear spectroscopic signals. My goal is to build a direct link between theory and experiment, to reveal the reaction mechanisms of photophysical and photochemical processes, and finally to provide important theoretical guidance for the design of efficient optoelectronic devices.

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Ultrafast Dynamics Simulations Accelerated by Machine Learning Models

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Photochemical reactions and photophysical processes occur on time scales ranging from femtoseconds to picoseconds. Although non-adiabatic dynamics methods can provide insight into the evolution of excited electronic states, traditional approaches are limited by the high cost of electronic structure calculations. To address these challenges, we have recently developed machine learning-based potential energy surfaces (PESs) and time-series models.[1] The former integrates neural network parameterized PESs with the time-dependent Baeck-An method to simulate the photo-induced isomerization in confined spaces.[2] The latter employs neural networks to learn the relationship between energy differences between electronic states and non-adiabatic couplings, effectively predicting excited-state dynamics and enhancing simulation efficiency. The development of these models will assist us in the exploration of more complex systems and improving the efficiency of studying excited-state dynamics processes.

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AI4Science: Quantum dissipative dynamics in the age of machine learning

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Open quantum systems play a vital role in areas like quantum information, quantum memory, and energy transfer in photosynthesis. However, their complex nature makes exact characterization challenging. Traditional methods for investigating these systems are often limited by computational demands or an inability to fully capture quantum effects.

Recently, machine learning (ML) has shown promise in predicting quantum dynamics efficiently. Our research highlights ML's ability to speedup the propagation of quantum dynamics based on a short history.[1] In addition, we also demonstrate that we can bypass the need for historical data, enabling the prediction of future quantum states based solely on time and/or simulation parameters.[2,3] We've developed the open-source MLQD package[4] and the QD3SET-1[5] database to support these advancements, alongside a study comparing 22 ML models for simulating open quantum systems.[6] Moreover, we have proposed an approach to enforced physical constraints in ML-based quantum dissipative dynamics.[7]] In my talk, I will provide a detailed overview of these developments and their implications.

Keywords: Open quantum systems, Quantum dissipative dynamics, Machine learning

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Concerted Phenomena on Chemical Reactions at Nano-Scale and Mechanics at Meso-Scale in Friction and Wear Processes Revealed by Large-Scale Molecular Dynamics Simulations

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In recent years, maximizing energy utilization efficiency in automobiles, airplanes, industrial robots, etc. is required due to strong demands for energy saving and carbon neutrality. To realize the above tasks, super-low friction and super-low wear technologies have become urgent social issues. A lot of nano-scale simulations on friction and wear processes have been done by molecular dynamics approaches and a lot of meso-scale simulations on the same processes have been done by continuum mechanics approaches. However, understanding friction and wear processes at each individual scale is not enough for designing and maximizing the friction performances because friction and wear processes are concerted phenomena of the chemical reactions at nano-scale and the mechanics at meso-scale.

Therefore, in the present study, we developed an in-house large-scale molecular dynamics code “Laich” to simulate the concerted processes of the chemical reactions at nano-scale and the mechanics at meso-scale in the friction interfaces. For example, we succeeded in clarifying the concerted processes of the chemical-reaction-induced mechanics and mechanics-induced chemical reactions at diamond-like carbon interfaces [1,2]. In the conference, our recent approaches for revealing and designing the friction and wear processes at both nano- and meso-scale will be presented.

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Understanding and predicting superionic Li-ion transport in amorphous halides

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In this talk, I will discuss our recent work in applying machine-learning force fields, trained on-the-fly from ab initio molecular dynamics (AIMD), to understand and predict superionic Li-ion transport in amorphous halides. We validated our approach by obtaining highly accurate simulated activation energies of Li-ion transport in $LiTaCl_6$ [1] and $LiNbCl_6$. We further predict that the activation energy of Li-ion transport will be as low as 0.144 eV and the ion conductivity will be as high as 15.7 mS/cm at room temperature for $LiNb_{0.5}Ta_{0.5}Cl_6$ [2]. Both values will be a record for halide-based electrolytes and solid electrolytes in general. Li-ion mobility is found to correlate with the degree of anharmonic cation-anion coupling. Despite the many similarities between Nb and Ta, this work demonstrates that when both are present, the synergy between Nb and Ta can lead to even higher superionic Li-ion conductivity in $LiNb_{0.5}Ta_{0.5}Cl_6$ than in $LiTaCl_6$ and in $LiNbCl_6$.

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Out of the Crystalline Comfort Zone: Tackling Working Interfaces with Machine Learning

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Machine learning (ML) promises a significant enhancement of multiscale modeling capabilities in the context of energy conversion and storage (ECS). In particular, ML interatomic potentials (MLIPs) trained with first-principles data already offer orders of magnitude speed-ups in the computation of predictive-quality energies and forces in atomic-scale simulations. This new efficiency finally allows to heads-on tackle the highly dynamic evolution of working interfaces in ECS systems, where the targeted functionality like catalytic activity or ion mobility both inherently drives and results from ongoing substantial structural, compositional and morphological changes. Unable to fully capture such operando evolution, direct first-principles based multiscale modeling focused hitherto on model (single-)crystalline surfaces or interfaces, where the system dynamics was typically restricted to select reacting or diffusing species that were considered central for a targeted primary function. The MLIP-enabled enhanced sampling capabilities instead allow to assess the thermodynamic stability of complex, possibly amorphous configurations and thereby establish reliable structural models for the working interfaces. Automated process exploration in turn provides more systematic access to the elementary steps that drive the operando evolution, paving the way for microkinetic simulations that analyze the entanglement of this evolution with the primary function. Obviously, these advances in modeling capabilities now call for ever more ML methodology, to efficiently analyze (trajectory) data from simulation cells containing thousands of atoms, to compute spectroscopic fingerprints or to extract refined descriptors for operando-evolution aware high-throughput virtual screening.

Reduced-scaling coupled-cluster method using cluster-specific virtuals

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Reduced-complexity representation of the coupled-cluster (CC) wave operator is obtained by using cluster-specific virtual (CSV) orbitals which can be viewed as the generalization of the well-known pair-natural orbitals. The increased algorithmic complexity of the CSV-based many-body methods is addressed by the nested tensor ("tensors-of-tensors") algebra support in the TiledArray tensor framework and by the development of fully-automated symbolic derivation and evaluation of the equations of CSV-based methods. In this talk we will report preliminary implementation and assessment of the CSV-CC methods.

Open-source framework for community validation of fragment-based quantum chemistry

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Abstract

Fragment-based methods represent an attractive way to circumvent the nonlinear scaling of conventional quantum chemistry and thereby apply high-level *ab initio* methods to systems of unprecedented size. Although a menagerie of fragmentation methods have been reported in the literature, most are minor variations on a small number of themes, yet head-to-head comparisons between them are rare. This is primarily a software limitation, as these methods are mostly limited to research-group codes or else are specific to a single quantum chemistry platform. This situation precludes the sort of community validation that has historically been the hallmark of quantum chemistry software development, where various models are implemented across multiple codes and results reported by one research group can be reproduced in other codes, down to the level of machine precision. The author's group has pioneered side-by-side comparisons of various fragmentations methods using a flexible software framework that interfaces with numerous quantum chemistry codes including (at present) CP2K, GAMESS, MOPAC, NWChem, ORCA, PySCF, Q-Chem, and xTB. These comparisons have allowed us to establish unifying principles for fragment-based algorithms and to target reproducible and systematically convergent results. Our fragmentation code has recently been rewritten in Python and released under an open-source license. Modification is simple enough to provide undergraduate research projects but it is also a powerful research tool that moves fragment-based methods closer to the reproducible standard of "model chemistries". Various validation tests will be described that establish what are essential and non-essential elements of a reliable and accurate fragment-based approach.

Combining the Many-Body Expansion and Subsystem-DFT

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The many-body expansion (MBE) offers an attractive approach for the treatment of large molecular systems, such as molecular clusters and crystals or proteins and protein–ligand complexes, with quantum-chemical methods. By combining the MBE with concepts originating from subsystem DFT, we have recently established a density-based many-body expansion (db-MBE) as a promising approach for the accurate, yet efficient treatment of large molecular systems [1].

In this talk, I will highlight recent applications of the db-MBE to water clusters [2] and ion-water clusters [3] as well as first applications of the db-MBE in combination with coupled cluster methods [4]. These examples show that already a density-based two-body expansion is able to reproduce interaction energies per fragment within chemical accuracy, and is able to accurately predict the energetic ordering as well as the relative interaction energies of different isomers of water and ion-water clusters. The extension to proteins and protein–ligand interaction energies [5,6] will also be discussed.

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Making and breaking electronic structures: lessons from embedding and machine learning

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The most enthusiastic modeler claims to accurately predict chemical reaction thermodynamics, kinetics, and nonequilibrium dynamics. Unfortunately, current models, while more robust and predictive than in past years, are often either too approximate or too expensive to provide a faithful representation of reality. Thus, it is imperative to develop new-generation electronic structure methods to aid experiments, as these face different yet similarly difficult circumstances. The talk introduces models based on orbital-free density-functional theory (OF-DFT), machine learning and density embedding to tackle large molecular condensed-phase systems that are too extensive for conventional electronic structure methods. To achieve chemical accuracy, nonstandard workflows are presented. These involve the dynamic combination of OF-DFT and conventional DFT methods, resulting in black-box-like adaptive embedding methods where molecular fragments are merged and split dynamically along a Born-Oppenheimer dynamics trajectory. The presented methods are available to the broader community as open-source Python implementations, such as Quantum ESPRESSO in Python (QEpy, qepy.rutgers.edu), OF-DFT software (DFTpy, dftpy.rutgers.edu), and density embedding software (eDFTpy, edftpy.rutgers.edu). The argument is made that with such a software arsenal at our disposal, we are ready to tackle the most difficult and timely electronic structure challenges available today.

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Towards realistic simulation of material with Ab initio quantum embedding

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At present, Moore's Law is gradually failing, and various new computing architectures are emerging one after another. Quantum computing is likely to be a revolutionary technology in the future and has recently exhibited great potentials in predicting chemical properties for various applications in drug discovery, material design, and catalyst optimization. However, current quantum computer can only limited around 20 qubits for chemistry simulation due to the limited coherence time and gate fidelity and so on.

In this talk, we shall present our work towards the larger scale and realistic chemistry simulation. Particularly, combine with quantum embedding theory, density matrix embedding theory as an example, we have greatly enhanced the ability of the current quantum device to simulate complex transition oxygen system such as NiO which only requires 20 qubits which may require almost 10k qubits vice versa.

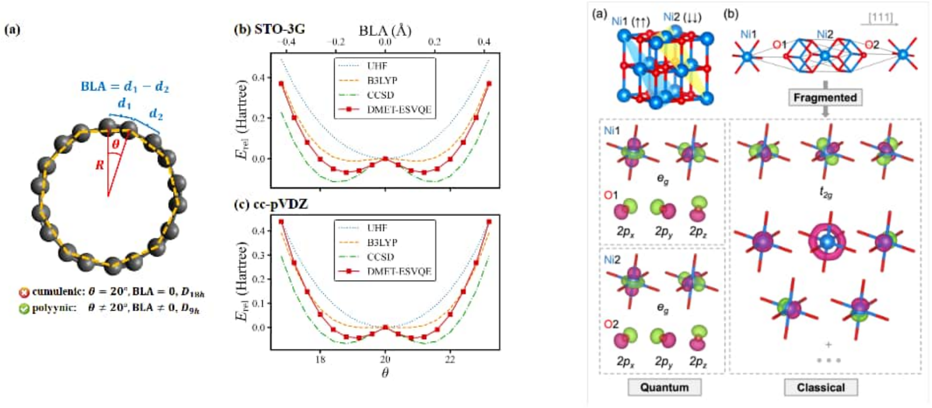

Figure1. C18 Stable Structure Prediction and NiO AFM-FM gap

Besides, I will also discuss our latest results with the highly GPU-accelerated quantum embedding package and our latest results on the water adsorption on graphene calculation, which paves the way towards realistic simulation of molecule and material.

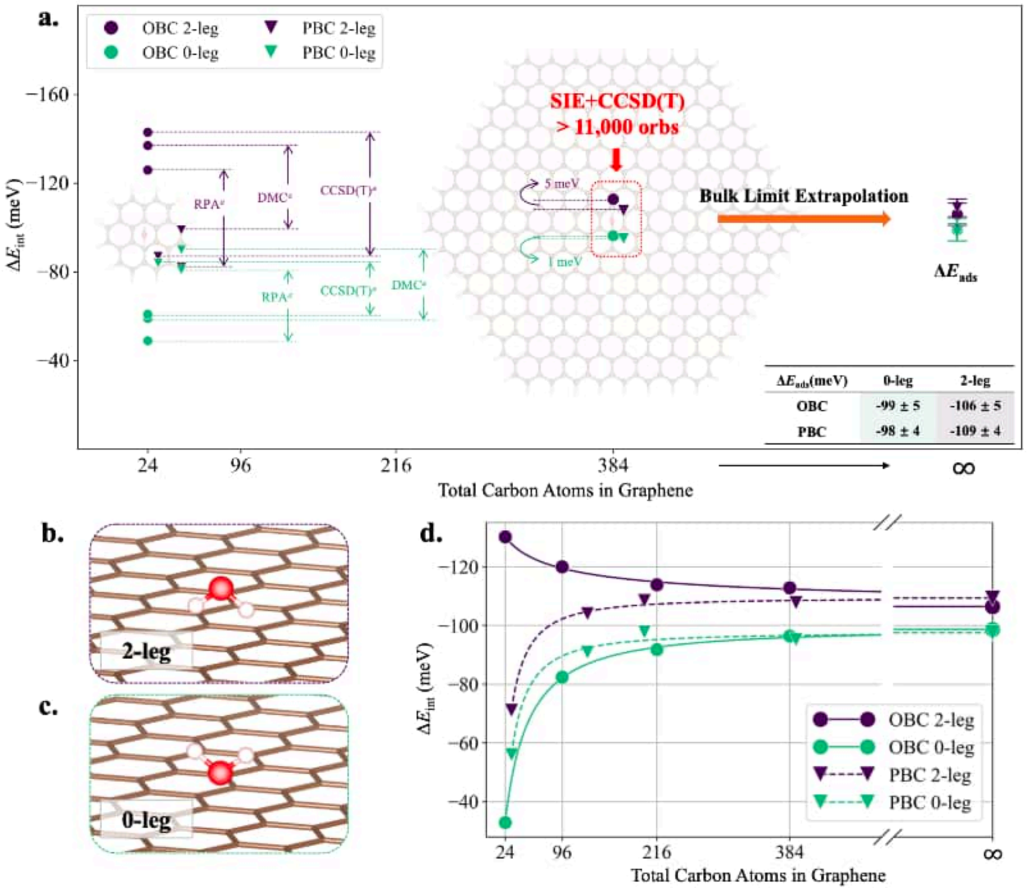

Figure2. Results on water adsorption on graphene

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Dynamic Ansatz Construction Utilizing Generative Machine Learning for Molecular Energetics in Noisy Quantum Hardware

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Quantum computing provides a promising framework for computing molecular wavefunctions and energies, efficiently addressing the exponential scaling issues that limit classical methods[1]. However, the noise in the current quantum hardware makes it unsuitable for practical applications[2].

A leading approach to minimize the impact of hardware errors is to dynamically tailor and deploy a concise yet highly adaptable ansatz[3,4]. We leverage generative machine learning, specifically the Restricted Boltzmann Machine (RBM), and many-body perturbative techniques to construct a shallow-depth chemistry-inspired ansatz[5]. By training on low-rank determinants derived from an approximate wavefunction, RBM predicts the key high-rank determinants that dominate the ground-state wavefunction. A shallow depth ansatz is constructed to explicitly incorporate these dominant determinants after dynamically decomposing them into low-rank components and applying many-body perturbative measures for further screening. The shallow depth of the ansatz makes it particularly well-suited for use on current noisy quantum hardware. Additionally, the proposed strategy for ansatz construction minimizes the requirements for quantum measurements. Our approach can be efficiently combined with state-of-the-art Neural Error Mitigation (NEM)[6], drastically enhancing its practical applicability.

We further incorporate Bayesian hyperparameter optimization for the RBM which allows us to leverage only a single step of RBM training and generation to move to the next perturbative rung of excitation operators. This leads to a reduction in classical cost overhead associated with our approach. We rigorously analyse the impact of initial parameters on the variational optimization of ansatz parameters, identifying local minima and barren plateaus, and suggesting optimal starting points for accurate energetics. The ansatz is tested across various molecules to evaluate its efficacy, with a detailed examination of its convergence trajectory. Its performance under noise is also evaluated. This approach facilitates the efficient computation of molecular energies and related properties, paving the way for exploring new chemical phenomena with near-term quantum computers.

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Quantum Algorithms for Electronic Structure Calculations

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Quantum technology may lead to a revolution of computation. In this talk, we focus on how to solve the electronic structure problem with a quantum computer. New quantum algorithms are developed to predict electronic structure of periodic systems [1,2]. A quantum circuit model is designed to represent matrix product state, which can generate exponentially large bond dimension compared to the density matrix renormalized group method [3]. Inspired by the quantum neural network, we also propose a new hardware heuristic wavefunction ansatz where its expressibility can be improved by increasing either the depth or the width of the circuit [4]. A software named Q2Chemistry is developed as a platform for quantum computational chemistry studies [5-11].

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Simulating Open Quantum System Dynamics on NISQ Computers with Generalized Quantum Master Equations

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We present a quantum algorithm based on the generalized quantum master equation (GQME) approach to simulate open quantum system dynamics on noisy intermediatescale quantum (NISQ) computers [1]. This approach overcomes the limitations of the Lindblad equation, which assumes weak system− bath coupling and Markovity, by providing a rigorous derivation of the equations of motion for any subset of elements of the reduced density matrix. The memory kernel resulting from the effect of the remaining degrees of freedom is used as input to calculate the corresponding non-unitary propagator. We demonstrate how the Sz.-Nagy dilation theorem can be employed to transform the nonunitary propagator into a unitary one in a higher-dimensional Hilbert space, which can then be implemented on quantum circuits of NISQ computers. We validate our quantum algorithm as applied to the spin-boson benchmark model by analyzing the impact of the quantum circuit depth on the accuracy of the results when the subset is limited to the diagonal elements of the reduced density matrix. Our findings demonstrate that our approach yields reliable results on NISQ IBM computers. Furthermore, I'd like to introduce QuCloud, provided by QUDOOR, which is an integrated cloud platform offering quantum computers, simulators, and programming environments for quantum algorithm design, research, and application exploration. QUDOOR's 20-qubit trapped ion quantum computing system [2] is opened to chemists from both academic and industry to facilitate and accelerate researches in chemistry.

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Water Trimer: Intermolecular Vibration-Tunneling States and Low-Frequency Spectrum from High-Dimensional Quantum Calculations

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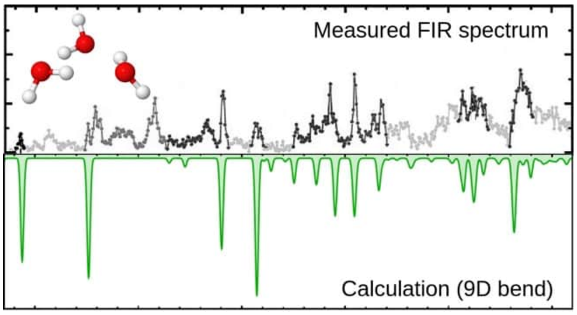
Water trimer is of fundamental importance as the smallest water cluster in which the nonadditive three-body interactions arise. They play a key role in shaping the structural, dynamical, and spectroscopic properties of liquid and solid phases of water and aqueous solutions. The trimer has 12 coupled large-amplitude intermolecular vibrational degrees of freedom (DOFs), and 9 intramolecular DOFs. The complexity of their quantum dynamics is greatly increased by the presence of two low barrier tunneling pathways, which give rise to elaborate patterns of tunneling splittings. I will present our newly developed methodology for rigorous 9D quantum calculations of the coupled intermolecular bending states and tunneling splittings of $(H_2O)_3$, for rigid monomers and fixed intermonomer distances [1]. The calculations encompass excited librational and torsional vibrations of the trimer, and the G_{48} molecular symmetry group of water trimer is fully exploited. The spectrum of the low-frequency vibrations of water trimer simulated using the eigenstates of the 9D bend Hamiltonian agrees remarkably well with the experimental far-infrared (FIR) spectrum of the trimer in helium nanodroplets measured by Havenith, Bowman, and co-workers, over the entire frequency range of the measurements from 70 to 620 cm^{-1}, as evident from the figure. Moreover, the ground-state torsional tunneling splittings from these 9D calculations are in excellent agreement with the spectroscopic data. 12D (rigid monomer) quantum calculations, which include also the intermolecular stretching vibrations fully coupled to the bending modes, are under way. We anticipate presenting the 12D results at this conference as well, which provide a complete description of the intermolecular vibrational states of $(H_2O)_3$.



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Dissipatons as generalized Brownian particles in open quantum systems

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Dissipaton equation of motion (DEOM) [1,2] is a fundamental theory for open quantum systems, which explicitly treats both the reduced system and hybrid-bath (or solvation) dynamics. This is a second-quantization theory and generalizes the well-established HEOM formalism [3]. The latter is equivalent to the Feynman-Vernon influence functional path-integral dynamics [4], with the focus on the reduced system quantities only. Dissipatons are generalized Brownian particles [5] that describe the influence of environments, as supported by the unified dissipaton algebra [1,2] and the dissipaton thermofield theory [6]. These enable the accurate DEOM evaluations on such as quantum transport [7], noise spectrum [8], and non-equilibrium thermodynamics problems [9], in strongly correlated fermionic and/or bosonic systems. Recent developments include further an exact dissipaton-embedded quantum master equation second-quantization theory [10].

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Vibronic spectra at non-zero temperatures from coherence thermofield dynamics

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I will present several methods for evaluating vibrationally resolved electronic spectra at nonzero temperatures based on the coherence thermofield dynamics [1], which converts the "hard", nonzero-temperature problem to an "easy" zero-temperature problem. We first transform the von Neumann evolution of the coherence component of the density matrix to the Schrödinger evolution of a "thermal" wavefunction in an augmented space with twice as many degrees of freedom. In the exact quantum approach [2], the thermal wavepacket is then propagated by solving the standard, zero-temperature Schrödinger equation with the split-operator Fourier method. To apply the method to realistic molecules, we combine it [1] with the on-the-fly ab initio extended thawed Gaussian approximation, which accounts exactly for mode distortion, Duschinsky rotation, and Herzberg-Teller effects and partially for anharmonicity. Compared to the zero-temperature case, the finite-temperature calculation requires no additional ab initio electronic structure calculations. We apply the extended Gaussian thermofield dynamics to evaluate the symmetry-forbidden absorption spectrum of benzene, where all of the aforementioned effects contribute [1]. Finally, I will show an extension to two-dimensional vibronic spectroscopy [3].

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Synthesizing first-principles simulation, machine learning, and experimental strategies for the design and analysis of a new class of high-performance battery electrolytes exploiting the Grotthuss structural diffusion mechanism

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Reliable theoretical prediction of complex chemical processes in condensed phases requires an accurate quantum mechanical description of interatomic interactions. If these are to be used in a molecular dynamics calculation, they are often generated "on the fly" from approximate solutions of the electronic Schrödinger equation as the simulation proceeds, a technique known as *ab initio* molecular dynamics (AIMD). However, due to the high computational cost of these quantum calculations, alternative approaches employing machine learning methods represent an attractive alternative and have become increasingly popular. As the adoption of machine-learning potentials becomes more widespread, it is important to consider how simulations employing them should be carried out. Specifically, as they do not implicitly include nuclear quantum effects, these effects must be treated explicitly, for which the most efficient approach involves the use of Feynman path integral techniques. This is especially important for processes involving light elements. In this talk, I will discuss how state-of-the-art machine learning potentials can be combined with path-integral molecular dynamics to address a variety of challenging chemical problems that have unexpected quantum behavior. In particular, I will discuss a new class of battery electrolytes that, by harnessing their unusual quantum character, could lead to breakthrough performance. Discovery of the mechanism of charge transport in these systems could only be achieved by the development of an equivariant transformer network interatomic potential model. I will discuss new quantum techniques, including path integrals and Green's functions, we are developing for studying electronic charge transfer between molecular species and between molecules and electrode surfaces.

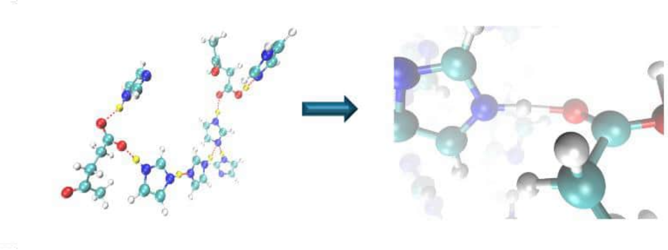

Figure 1. Chain structure in the new electrolyte and example of a proton transfer event.

Ab initio doorway-window methods for the simulation of nonlinear spectroscopic signals

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I will give a brief overview of the recently proposed methods for the on-the-fly simulation of femtosecond time-resolved transient-absorption pump-probe, electronic 2D, and visible pump – X-ray probe spectra with quasi-classical trajectories [1]. The methods are based on the simulation protocol which employs the classical doorway-window representation of third-order 4-wave-mixing signals and accounts for the finite duration and spectral shape of the laser pulses involved. I will also discuss feasibility of the extension of these methods towards simulation of 6-wave-mixing and strong-field signals.

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ULTRAFAST PROCESSES: A NEXT GENERATION QTAIM INTERPRETATION

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We discuss a variety of recent ultra-fast applications analysed using Next Generation Quantum Theory of Atoms in Molecules (NG-QTAIM) for both molecules and the solid state. This is undertaken using pairs of left- and right-linearily or circularly or elliptically polarized laser pulses on femtosecond or faster time-scales. The carrier-envelope phase (CEP) angle ϕ is varied to learn more about learn more about the relationship $\rho(\mathbf{r}) \rightarrow \boldsymbol{\psi}(\mathbf{r})$.

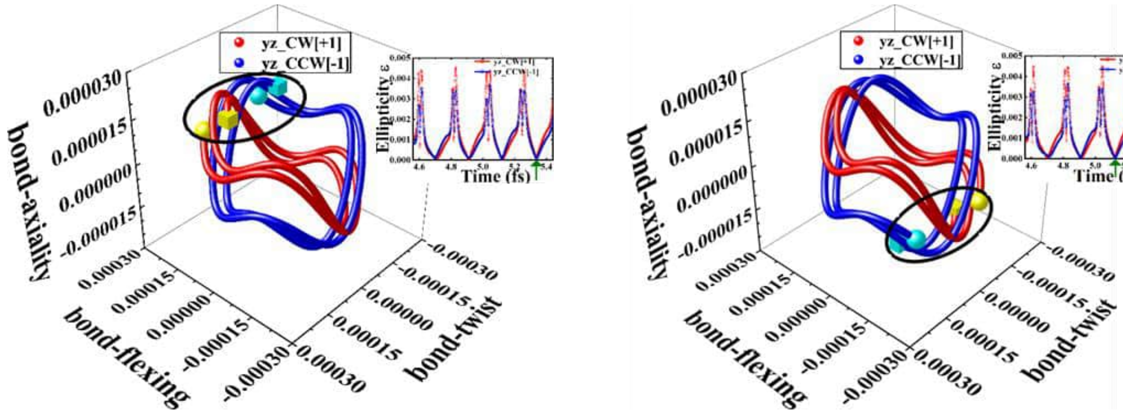

Figure 1: **Left**. The ethane C1-C2 *BCP* Hessian of $\rho(\mathbf{r})$ eigenvector-following trajectories $\mathbb{T}_{\mathbf{F}}(s)$ for the right-handed, clockwise (**CW[+1]**) and left-handed, counter-clockwise (**CCW[-1]**) circularly polarized laser pulses of duration 10 femtoseconds for the carrier-envelope phase (CEP) angle $\phi = 0.0°$ corresponding to the electric field $\mathbf{E} = 200.0 \times 10^{-4}$ a.u., see the main text for further explanation. The start and end of each $\mathbb{T}_{\mathbf{F}}(s)$ are denoted by balls and cubes respectively and are surrounded by an ellipse. **Inset**. The corresponding variation of the ethane C1-C2 *BCP* ellipticity ε, notice the position of the green arrow on the *x*-axis.
Right. The corresponding ethane C1-C2 *BCP* $\mathbb{T}_{\mathbf{F}}(s)$ for the CEP angle $\phi = 180.0°$. Notice the changed position of the black ellipse relative to the left figure. **Inset**. The corresponding variation of the ethane C1-C2 BCP ellipticity ε, notice that the green arrow on the *x*-axis has moved leftwards relative to that of the left inset.

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Quantum control of ultracold atom-ion and atom-molecule collisions

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Experiments at ultralow temperatures provide unprecedented opportunities for preparing reagents in well-defined quantum states and controlling their collisions with external fields. I will present our recent results of *ab initio* electronic structure and multichannel scattering calculations proposing, guiding, and explaining ultracold experiments. I will start with our efforts related to hybrid systems of laser-cooled trapped ions and ultracold atoms combined in a single experimental setup. In collaboration with experimental groups in Amsterdam and in Freiburg, we reached and explained the quantum regime of ion-atom collisions manifested via shape resonances [1] and their quantum control with an external magnetic field observed with magnetic Feshbach resonances [2]. I will continue by explaining the mechanism of recently observed magnetic Feshbach resonances in ultracold Na+NaLi atom-molecule mixtures [3]. In collaboration with groups at MIT and in Nijmegen, we showed that these Feshbach resonances result from spin-rotation and spin-spin couplings in combination with the anisotropic atom-molecule interaction. I will conclude by discussing hyperfine-to-rotational energy transfer in ultracold Rb+KRb atom-molecule collisions [4]. In collaboration with groups at Harvard and in Reno, we found that electronic spin is strongly coupled with molecular rotation in this system.

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Tuning Range Separated Hybrids for the description of excited states

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In this contribution we will present different procedures for Tuning Range Separated Hybrids focusing on their accuracy for the description of both Local (LE) and Charge Transfer (CT) excited states.

In particular, both the method originally proposed by Stein, Kronik and Baer leading to the so called Optimally Tuned RSH (OT-RSH) and a novel methodology based on the use of the computed effective electron-hole distance to tune the range-separation parameter, γ, will be presented.

Our aim is to propose a way to define novel Density Functional Approximations that keep the optimal accuracy of global hybrid for local excited states and cure their misleading behavior leading to underestimate the energy of CT states of inter- and intra-molecular character. To this end, while keeping a strict respect of the exact asymptotic behavior obtained by imposing full HF exchange at long range, we propose to tune the range-split parameter depending on the hole-electron separation computed for the CT state of interest. Ultimately, this non-empirical procedure enables to define a system dependent range separation parameter optimal for the treatment of both CT states and LE excited states.

Advancements in MRSF-TDDFT: Addressing the Limitations of DFT/TDDFT

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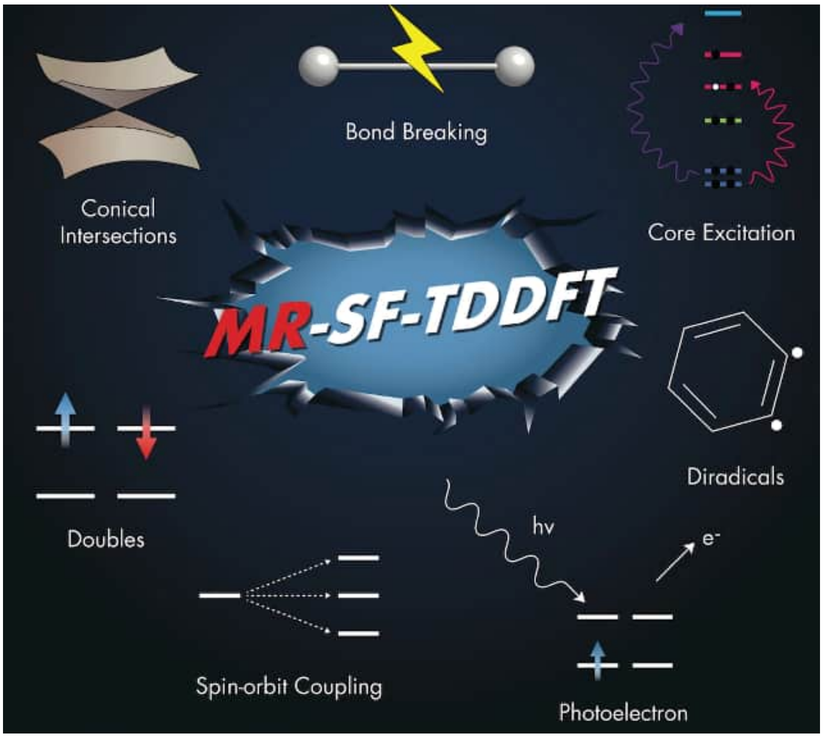
Density Functional Theory (DFT) and Linear Response Time-Dependent DFT (LR-TDDFT) are essential tools for routine computational chemistry. However, DFT's single reference formulation struggles with accurately describing open-shell singlet systems, such as diradicals and bond-breaking scenarios. Similarly, LR-TDDFT faces challenges in modeling conical intersections, doubly excited states, and core-level excitations. This talk demonstrates that many of these limitations can be addressed by the recently developed Mixed-Reference Spin-Flip TDDFT (MRSF-TDDFT). This method offers an accurate alternative for these challenging situations. By leveraging the practicality of LR formalism, MRSF-TDDFT is poised to become a key tool for routine computational tasks.



Modern density functional approximations are ill-designed to compute molecular properties

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We show that properties of molecules with low-frequency modes calculated with density functional approximations (DFAs) suffer from spurious oscillations along the nuclear displacement coordinate [1]. Occasionally, the problem can be alleviated using extensive integration grids that compromise the favorable cost-accuracy ratio of DFAs. Since spurious oscillations are difficult to predict or identify, DFAs are exposed to severe performance errors in IR and Raman intensities and frequencies and other molecular properties [2,3]. Using Fourier spectral analysis and digital signal processing techniques, we identify and quantify the error due to these oscillations for 45 widely used DFAs, and indicate whether the exchange or correlation functionals are responsible for it [4]. Finally, we show that spurious oscillations occur because exchange-correlation energy DFAs are ill-designed, exhibiting local spurious oscillations in the exchange-correlation energy density. We present a judicious modification of B97 and ωB97XD functionals, which drastically reduces spurious oscillations preserving the accuracy of the original functionals [5]. The latter strategy can be applied to the design of modern DFAs that do not suffer from this problem.

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Density Functional Theory on Quantum Computers

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Quantum computers have shown promises to solve problems that are currently intractable on classical computers. While quantum chemistry has been identified as the killer applications of quantum computers in the near term, the focus is on wavefunction theory that provides an exact solution to the quantum problem. However, the applications of wavefunction theory is limited in terms of the size of affordable systems, even on quantum computers. Currently, computations on large systems rely mainly on density functional theory, for which no quantum advantage has been envisioned so far. In this talk, we question this a priori by investigating the benefit of quantum computers to scale up not only many-body wavefunction methods, but also density functional theory, and consequently the whole range of application of quantum chemistry [1]. The Kohn-Sham equations are solved by the so-called *ensemble variational quantum eigensolver* [2-4], recently used to get a democratic description of ground and excited states on quantum computers.

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NHC-cracker: A Platform for the Engineering of N-Heterocyclic Carbenes for Diverse Chemical Applications

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N-heterocyclic carbenes (NHC) are versatile molecules with applications spanning from catalysis to materials science. Selecting the best NHC for a specific purpose traditionally relies on human expertise to summarize the vast literature on NHCs. In this work, we introduce a machine learning-based workflow capable of identifying potentially promising NHCs. To this end, we developed the NHC-cracker database, which contains over 200 descriptors for 1,871 non-redundant NHCs, each documented as an NHC-metal complex in the Cambridge Structural Database.

To demonstrate the utility of the NHC-cracker database, we implemented a multiscale experimental/DFT/ML workflow to identify promising NHCs for a challenging photoredox reaction. Starting with five experimental data points, we created a dataset of 47 NHCs based on DFT calculations and trained a multivariate linear regressor. To validate the capability of a regressor trained on a few-entry dataset, to predict catalysts with performances beyond those of known catalysts, we developed a series of tests. These tests are condensed into a confidence score aimed at estimating the expected prediction capability of a new model. To achieve robust validation of these tests we applied them to 29 reaction classes assembled from literature. The validated regressor was then used to screen all NHCs in the NHC-cracker database, identifying candidates that could potentially yield high experimental yields. The same approach could be extended to the design of NHCs for developing functional materials.

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Mechanism-based organometallic catalyst design: a hole in the ice

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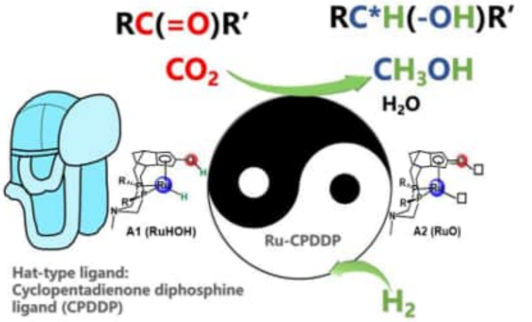
This talk will summarize our group's research works on the rational design of organometallic catalysts based on reaction mechanisms, which involves transition-metal complexes with designed pincer, bowl-type, hat-type and cage-type ligands for the hydrogenation, hydroformylation etc..[1] These works might provide theoretical insights into the mechanism-based rational catalyst design aiming on realizing atomic efficiency, high catalytic activity and high selectivity, and facilitate the development of industrial catalysts integrating with current chemical industries.



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Stretching the limits of surface reactivity: mechanochemistry and topological catalysis

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For the past century and more, physical chemists and chemical physicists have sought to understand chemical reactivity in terms of underlying physical processes. This fruitful connection has led to great breakthroughs in conceptual understanding and practical application for fostering and controlling chemical reactions. Here, we examine how the physical principles of solid mechanics and topological physics can influence surface chemistry.

Mechanochemistry: The field of mechanochemistry is presently experiencing a renaissance. The governing hypothesis of this field is that force and stress (delivered by adjacent materials) can open novel avenues of chemical reactivity. In this context, we recently developed methodologies to relate applied pressure to molecular chemical transformations. More recently, we have examined the chemical consequences of bending nanomaterials. This deformation rearranges electronic states spatially, creating new opportunities for chemical reaction. Following this paradigm, we demonstrated that molecules bonded to curved graphene will definitively move, with the direction of movement controlled by the sign of the curvature and the type of molecular bonding. We also explored the strain-driven water decomposition on graphene as a model system to investigate the influence of mechanical distortions on 2D materials.

Topological physics: Over the past twenty years, physicists have come to appreciate that the band structures of crystals can have different connectivities in momentum space, and some of these connectivities (“topologically nontrivial”) are not adiabatically connected to isolated connections of atoms or molecules. Thus, in some deep ways, the band topology encodes the nature of the chemical bonding in materials, leading to novel, potentially chemically active, edge states. In this area, we predicted novel topological band features, which have been experimentally realized. More recently, we have developed theoretical insights into how specific topological surface behaviors can be related to catalytic enhancements of energy-relevant chemical reactions.

These findings provide new avenues for the manipulation of molecular motions and chemical interactions via mechanical deformations of various two-dimensional materials and the exploration of surfaces in topologically novel materials, broadening the palette of physical phenomena that can beneficially impact surface chemical reactivity.

The authors acknowledge the support of the NSF through grant CHE-2303044 and the DOE through grant DE-SC0024942, as well as computational support from NERSC.

Converging High-Level Coupled-Cluster Energetics with Semi-Stochastic, CIPSI-Driven, and Adaptive CC(*P*;*Q*) Methods

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It is well established that the exponential wave function ansatz of coupled-cluster (CC) theory and its extensions to excited, open-shell, and multireference states are among the most efficient ways of incorporating many-electron correlation effects in molecular applications. In this talk, we will discuss novel ways of obtaining accurate energetics equivalent to high-level CC and equation-of-motion (EOM) CC calculations, such as CCSDT, CCSDTQ, and EOMCCSDT, at small fractions of the computational costs, even when electronic quasi-degeneracies become large and higher–than–two-body components of the relevant cluster and excitation operators become nonperturbative, which result from merging the moment expansions that define the CC(*P*;*Q*) framework [1] with Quantum Monte Carlo (QMC) propagations in the many-electron Hilbert space [2,3] and with the selected configuration interaction (CI) approach abbreviated as CIPSI [4,5]. We will conclude by highlighting the newest adaptive, self-improving, CC(*P*;*Q*) formalism, which frees us from the originally exploited active orbitals [1] and the more recently utilized non-CC (CIQMC, CIPSI) [2-6] or stochastic (CIQMC, CCMC) [2,3,6] concepts by taking advantage of the intrinsic mathematical structure of the CC(*P*;*Q*) moment expansions in defining the underlying excitation manifolds [7]. The usefulness of the semi-stochastic, CIPSI-driven, and adaptive CC(*P*;*Q*) methodologies will be illustrated by chemical bond dissociations and reaction pathways [2,4,5,7], singlet–triplet gaps in biradicals [5,6], and excited states including one- as well as many-electron transitions [3]. Information about the availability of CC(*P*;*Q*) methods in GAMESS and the open-source CCpy package [8] will be provided as well.

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Recent progress on the multireference electronic structure theory

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Due to the electronic degeneracy or quasidegeneracy, it is difficult for the single reference theory such as the closed shell Møller–Plesset perturbation theory (MP) [1] and the open shell perturbation theory (OSPT) [2,3] to be used to calculate excitation energies, to describe the dissociation behavior and to predict a chemical reaction when there are one or more bonds broken. In these cases, a multireference theory is required. Based on the Taylor expansion of a secular equation, the multireference perturbation theory (MRPT) [4] is derived in our previous work though it is not size extensive. Next, A size extensive and orbitally invariant multireference perturbation series (SMRPT) [5] is derived based on the Rayleigh–Schrödinger perturbation theory. Its computational cost is comparable to the single reference Møller–Plesset perturbation theory. Based on the complete active space multireference wavefunction, multireference Rayleigh–Schrödinger perturbation theory (MRSPT) [6] is derived with the assumption that the orbital energies of active orbitals are the same. MRSPT2 and MRSPT3 are size extensive.

Recently block effective Hamiltonian theory (BEHT) was developed in our group [7]. Configuration interaction functions are divided into P, Q and R spaces. Effective Hamiltonian is constructed with the partitioning technique within the P space. The eigenvalue problem of the effective Hamiltonian is then solved iteratively. The iteration numbers are all less than 10. The accuracy of BEHT is better than that of the second order multireference perturbation theory at almost the same level of computational amount. Numerical calculations show the good performances of BEHT in comparison with other theoretical methods.

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Alternative coupled cluster methods based on electron-pair theories

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Quantum-mechanical modeling can assist experimental studies in efficiently devising novel compounds with desired properties. However, the computational models are also difficult primarily because conventional highly-accurate quantum chemistry approaches are technically limited to small—and to some extent rather simplified — model compounds and demand user control on an expert level. We will discuss alternative wave-function-based approaches that represent computationally inexpensive, robust, and black-box-like electronic structure methods. Specifically, we will focus on electron-pair theories, where two-electron functions are the fundamental building blocks of the electronic wave function, and how they can be extended to obtain a balanced description of static/nondynamic and dynamic correlation. We will demonstrate how these inexpensive methods allow us to accurately and efficiently model building blocks of organic electronics.

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DMRG-tailored coupled cluster method in the 4c-relativistic domain

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Heavy atom compounds represent a challenge for computational chemistry, due to the need for simultaneous treatment of relativistic and correlation effects. Often such systems exhibit also strong correlation which hampers the application of perturbation theory or single-reference coupled cluster (CC) methods. As a viable alternative, we have proposed to externally correct the CC method using the density matrix renormalization group (DMRG) wave functions, yielding the DMRG-tailored CC method. This method has been successfully implemented and applied in the non-relativistic regime [1-5], and its multireference generalization has been recently developed [7]. In the work [6] we have reported a first implementation of this method in the relativistic context, which was restricted to molecules with real double group symmetry. Now we present a fully general implementation of the method, covering complex and quaternion double groups as well. The 4c-TCC method thus becomes applicable to polyatomic molecules including heavy atoms. For assessment of the method, we performed calculations of the chiral uranium compound NUHFI, which was previously studied in the context of the enhancement of parity violation effects. In particular, we performed calculations of a cut of the potential energy surface of this molecule along the dissociation of the N-U bond, where the system exhibits a strong multireference character. Since there are no experimental data for NUHFI, we have performed also an analogous study of the (more symmetric) NUF_3 molecule, where the vibrational frequency of the N-U bond can be compared with spectroscopic data.

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Downfolding in Atomic and Molecular Electronic Structure

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Quantum Chemistry is traditionally done by assuming a form for the wavefunction and optimizing parameters. Alternatively, one could ask the question whether the Hamiltonian operator itself could be modified. One could do this in an ad hoc manner, as is usually done (i.e. for semi-empirical methods), or one could seek a systematic method for this downfolding. We are exploring a method of downfolding introduced by Wilson and by Wegner, which has proven useful in nuclear physics by Bogner and coworkers. Formally, it is an Effective Field Theory built along Renormalization Group ideas. Besides discussing the mathematical model, examples from atomic and molecular physics will be given.

Basis-set limit correlation energies for large molecules with density-based basis-set corrections

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The calculation of the density-based basis-set correction (DBBSC) of Toulouse, Giner, and co-workers, which remedies the basis-set incompleteness (BSI) error of the correlation energy, is combined with local approximations. Aiming at large-scale applications, the procedure is implemented in our efficient local natural orbital-based coupled-cluster singles and doubles with perturbative triples [LNO-CCSD(T)] scheme. To this end, the range-separation function, which characterizes the one-electron BSI in space, is decomposed into the sum of contributions from individual localized molecular orbitals (LMOs). A compact domain is constructed around each LMO, and the corresponding contributions are evaluated only within these restricted domains. Furthermore, for the calculation of the complementary auxiliary basis set correction, which significantly improves the Hartree–Fock energy, the local density fitting approximation is utilized. The errors arising from the local approximations are examined in detail, efficient prescreening techniques are introduced to compress the numerical quadrature used for DBBSC, and conservative default thresholds are selected for the truncation parameters. The efficiency of the DBBSC-LNO-CCSD(T) method is demonstrated through representative examples of up to 1000 atoms.

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Complex-scaled electronic-structure methods for nonradiative decay processes

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The interaction of molecules with radiation can lead to metastable electronic states that decay non-radiatively by emission of electrons. This includes high-energy processes such as Auger decay [1] of core-ionized states, where electrons with energies of hundreds or even thousands of electron volts are emitted, as well as low-energy processes such as Coster-Kronig decay [2] and interatomic/intermolecular Coulombic decay,[3] where the emitted electrons have energies of a few or even less than one electron volt.

The theoretical modeling of nonradiative decay is difficult because the initial states are embedded in the ionization continuum and not L^2-integrable. An elegant approach to decaying states is afforded by complex scaling and the method of complex basis functions,[4,5] which produce Hamiltonians with complex eigenvalues from which total and partial decay widths can be extracted. Our numerical results indicate that complex-scaled coupled-cluster theory and Møller-Plesset perturbation theory are well suited for a broad range of autoionization phenomena.[6–10]

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Quantum-information-based orbital optimization, energy-filtered excited states and electron dynamics within the coupled cluster framework

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In this talk, I will present three new algorithms within the coupled cluster framework for optimizing orbitals using quantum information (QI) tools [1], obtaining excited states and carrying out electron dynamics within a specified energy window.

In the first part, I will show how QI tools, e.g. the total orbital entanglement entropy, can be used to quantify the complexity of a wavefunction. Based on this insight, we design an algorithm to minimize the entropy by rotating the orbitals, aiming at minimizing the representational complexity of the wavefunction and improving the accuracy of approximate ansatze such as the tailored coupled cluster singles and doubles.

In the second half, I will introduce two algorithms [3] for probing excited states within a specified energy window, based on the Cauchy integral formula (CIF). The original FEAST [2] algorithm was designed for finding all excited states within an energy window, and the key idea was using a contour integral representation of the spectra projector. I will show that it is a special case of the CIF and that any holomorphic functions of a diagonalizable operator can be written in the CIF form. This opens the door to a much broader class of algorithms that can be achieved in the CIF form. As examples, I will present an improved version of FEAST that can automatically identify the correct number of eigenstates and resolve them within a specified energy window in the EOM-CCSD framework. In addition, I will showcase as a proof of principle that the exponential time evolution operator in the CIF form can be used to accurately evolve states with extremely large time step sizes.

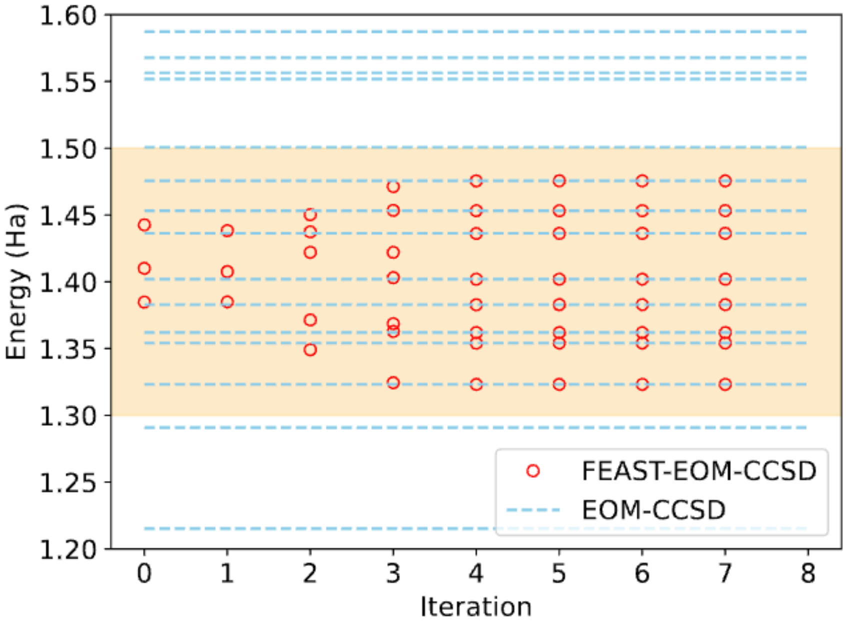

Figure 1: FEAST-EOM-CCSD correctly finds all the excited state energies within a specified energy window in the H2O molecule [3].

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Multireference density functional theory with valence bond methods

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In this talk, a hybrid density functional valence bond method based on unpaired electron density, called λ-DFVB(U), is presented, which is a combination of valence bond self-consistent field (VBSCF) method and Kohn–Sham density functional theory (KS-DFT). In λ-DFVB(U), the double-counting error of electron correlation is mitigated by a linear decomposition of the electron-electron interaction using a parameter λ, which is a function of an index based on the number of effectively unpaired electrons. Besides, λ-DFVB(U) is based on the approximation that correlation functionals in KS-DFT only cover dynamic correlation and exchange functionals mimic some amount of static correlation. The method is applied to test calculations of atomization energies, atomic excitation energies, and reaction barriers. It is shown that the accuracy of λ-DFVB(U) is comparable to that of CASPT2, while its computational cost is approximately the same as VBSCF. Furthermore, A multistate hybrid density functional valence bond method, called λ-DFVB(MS), is presented, in which an effective Hamiltonian matrix is constructed in the diabatic state basis obtained by the valence-bond-based compression approach for diabatization (VBCAD) scheme, and the interaction between electronic states can be included through the diagonalization of the effective Hamiltonian matrix.

Improving Density Functional Approximations through Exact Constraints and Exact Wave Function

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The present-day commonly used density functional approximations (DFAs) suffer from various systematic errors, and they can all be attributed to the violation of some exact constraints. Here we focus on yet another unexplored exact constraint, i.e., the semi-classical limit, where $\hbar \to 0$. Through a model atomic calculation, we show that the exact total energy as $\hbar \to 0$ saturates to a finite value, whereas the mainstream DFAs have qualitatively wrong divergent behavior of $\hbar^{-1/6}$. Moreover, we show that this semi-classical limit is highly relevant to strongly correlated systems such as in the stretching of chemical bonds, or transition metal diatomic molecules in their equilibrium bond length. By introducing an effective ħ for valence electrons, we estimate that the ħeff for such systems can be as small as 0.05. Thus, this exact constraint might inspire novel functional approximations for describing strong correlation. In the second part of the talk, we discuss our recently developed method for solving Schrödinger equations, which allows us to obtain the exact analytic structure of wave functions for one and two-body problems, and can be further generalized to many-body problems. The analytic expression of the ground state wave function is ultimately cast into an exact factorized form including a pre-exponential power factor, an exponential decaying term and a modulator, a mildly-varying and bounded function that can be easily approximated. This new analytic formula can be potentially a new starting point for developing DFAs that go beyond the single electron picture.

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Accurate ΔSCF from ensemble density functional theory

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I will introduce GX24 [1], an effective ΔSCF density functional approximation for ground (G) and excited (X) state prediction. GX24 (Figure 1) can out-perform TDDFT on excitation energy problems where TDDFT works, but also performs well for double and charged excitations where TDDFT fails completely. Its strong performance reflects the first principles “ensemblisation” strategy [i.e. use of exact constraints from ensemble density functional theory] employed in its design, which will also be summarised in the talk. GX24 includes the first (to my knowledge) general purpose approximation for density-driven correlations [2].

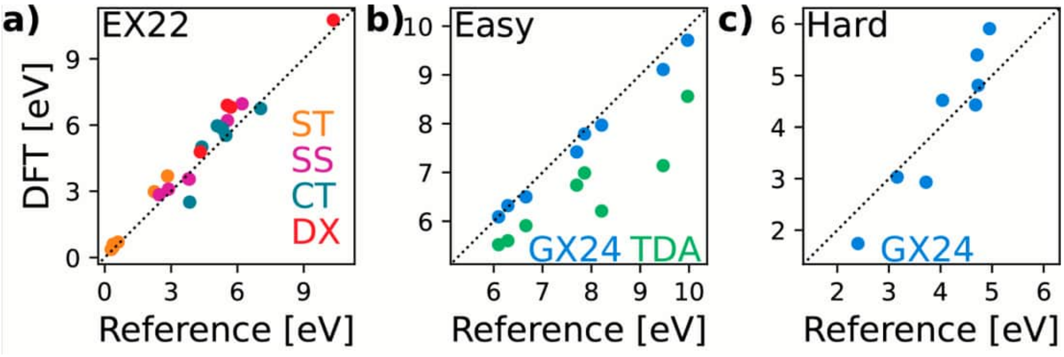

Figure 1. Performance of GX24 on excitations. a) a mixture of singlet-triplet (ST), singlet-singlet (SS), charge transfer (CT) and double excitations (DX); b) relatively easy SS excitations where TDDFT can work; and c) hard DX where TDDFT fails completely.

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Machine-Learning Atomic Simulation Resolves Active Site for Selective Ethene Epoxidation on Silver

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This lecture introduces our recent progress in machine-learning atomic simulations for catalysis by using LASP software (www.lasphub.com) developed by our group [1]. Our methodology for bulk, surface structure search, and reaction sampling in the grand-canonical ensemble will be overviewed [2-3]. These methods will recently be applied to resolve the active site for selective ethene epoxidation on silver, a long-standing problem in the field for more than 50 years. Ag-catalyzed ethene epoxidation is the only viable route for making ethene oxide (EO) in industry. Due to the lack of tools to probe the reaction at high temperatures and high pressures, the active site structure remains highly controversial. Here, with advanced machine-learning grand canonical global structure exploration and in-situ catalysis experiments, we identify a unique surface oxide phase, namely O5 phase, grown on Ag(100) under industrial catalytic conditions. This O5 phase features square-pyramidal subsurface O and strongly adsorbed ethene, which can selectively convert ethene to EO. The other Ag surface facets, Ag(111) and Ag(110), although also reconstructing to surface oxide phases, only produce CO2 due to the lack of subsurface O. The complex in-situ surface phases with distinct selectivity contribute to an overall medium (50%) selectivity of Ag catalyst to EO. Our further catalysis experiments with in-situ infrared spectrum confirm the theory-predicted IR-active C=C vibration (1583 cm^{-1}) of adsorbed ethene on O5 phase and the microkinetics simulation results. The active phase structure and activity help to settle the long dispute on the nature of active oxygen in ethene epoxidation caused by the “pressure gap” and shed light on the design of better catalysts for olefin epoxidation. [4]

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Advancing Realism in Catalytic Models: Modeling Active Sites on Nanoparticles

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Recent advancements in computational catalysis have shown great success, with predictive DFT models becoming routine in homogeneous catalysis and machine-learning-powered tools now capable of modeling complex heterogeneous catalytic reaction networks to drive catalyst design [1]. However, these models often omit the diversity and *in situ* transformations of active centers for computational feasibility.

This talk will address studies focusing on the transformation and diversity of catalytic active centers. Topics include the transformation of nanoparticle catalysts to solute species during coupling reactions [2], the superior activity of nanoparticle edges in aryl halide oxidative addition, compared to ideal surfaces [3], and the complexity of reaction networks for CO and CO_2 hydrogenation to C_1 and C_2 oxygenates due to the diversity of active sites. We will explore how extensive DFT modeling, combined with machine learning models and semi-empirical simulations—integrated into thermodynamic and kinetic models—aids in understanding experimental observations in these reactions.

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Electronic Effects on Gas-Phase C−H Bond Activations by Cluster Oxides and Metal Carbides: The Methane Challenge

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In this talk, I'll show you a dizzying mechanistic landscape of gas-phase methane C−H bond activation by a few metal cationic oxides (MCO) and carbides at ambient conditions. One mechanism is hydrogen atom transfer (HAT), which occurs whenever the MCO possesses a localized oxo radical $(M{-}O^{\bullet})$[1]. Whenever the radical is located on the metal centers as in $[Al_2O_2]^{\bullet+}$ the mechanism crosses-over to proton-coupled electron transfer (PCET).[2] Bare transition-metal carbides $[MC]^+$ cations (M = Sc – Zn and Au) act by three different mechanistic scenarios.[3] For example, Cu^+, performs coupling of C to methane to yield ethylene, in a single almost barrier-free step, with an unprecedented atomic choreography catalyzed by the OEF of Cu^+.[3b]

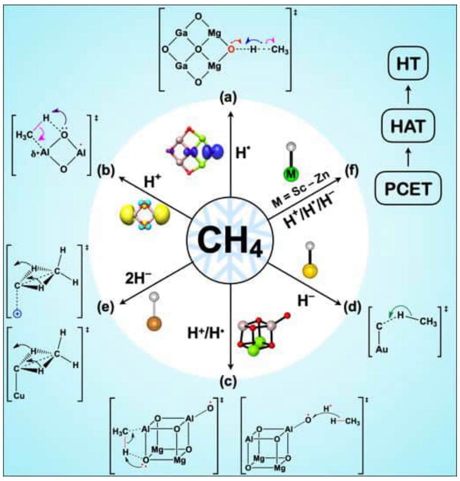

Figure 1. Mechanistic picture of methane C−H bond activation.

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Theoretical Design of Energy Catalysis

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Precision design and prediction of efficient energy catalytic materials urgently requires new theoretical guiding strategies. We first propose the concept that the surface orbital orientation at material interfaces influence the chemical reaction kinetics, offering a new theoretical approach for high-efficient material design. Simultaneously, we further develop the strategy of surface orbital energy effect on the reaction performance, overcoming the limitations of the d-band center theory application. Moreover, based on the surface orbital steric and energy effects, we innovated a material parameterization method FOGN independent on structural information, achieving the AI precise structure design nd reactivity prediction.

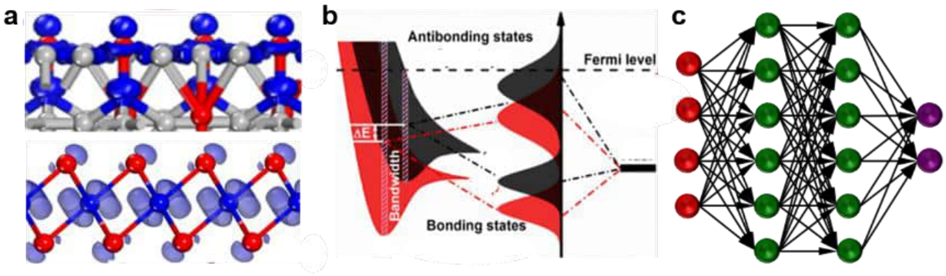

Fig. 1 Orbital steric (a) and energy (b) effects and AI design and prediction (c).

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Core and valence properties of heavy element species from relativistic (embedded) coupled cluster calculations

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Accurate electronic structure calculations have become an indispensable tool to understand the molecular properties of heavy and superheavy elements. Such approaches help make sense of the underlying complex physical processes probed by experiments, or in the case such experiments are unfeasible due to the heavy elements' radiotoxicity. In this presentation I will outline our contributions to developments of coupled cluster approaches based on two- and four-component Hamiltonians for valence and core spectra and their application to investigating species in the gas phase and in solution [1-3], as well as for the determination of linear and quadratic response properties [4, 5].

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Theoretical Studies of Coordination Structures and Electronic Spectra of Cm^{3+} Species at the Mineral-Water Interface

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Accurate interpretation and prediction of actinide coordination chemistry at the mineral-water interface is one of the key scientific issues that need to be urgently addressed in environmental radio-chemistry. However, due to the strong relativistic and electron correlation effects of actinides, as well as the high complexity of their interactions with mineral surfaces, high-precision theoretical calculations of actinides at mineral-water interface are extremely challenging. In particular, no theoretical studies of the electronic spectra of actinides at the mineral-water interface have been carried out. In this talk, the coordination structure, stability, and electronic spectral properties of Cm^{3+} sorption species at typical mineral-water interfaces have been accurately predicted by combing ab initio molecular dynamics simulations and wave function theory calculations, with the calculation results in good agreement with available experimental results. [1, 2]

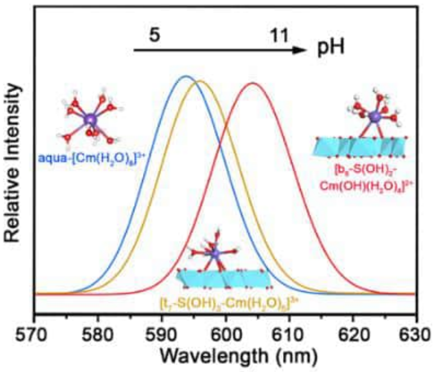

Figure 1. The simulated emission spectra of the Cm^{3+} species at the gibbsite-water interface.

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Development and Application of a Relativistic CASPT2/RASPT2 Program based on the DIRAC software

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Exploring electronic states in actinide compounds is a critical aspect of nuclear science. However, considering relativistic effects and electron correlation in theoretical calculations poses complex challenges. To address this, we developed a CASPT2/RASPT2 program alongside the DIRAC program [1], enabling calculations of electron correlation methods using multiconfigurational perturbation theory with various relativistic Hamiltonians. We currently employ a method that combines the Improved Virtual Orbital (IVO) approach with CASCI methodologies as reference functions, deviating from the traditional use of CASSCF. Additionally, we have implemented the RASCI-RASPT2 method to handle larger active spaces and have parallelized the entire program. We will introduce the program's overall structure, including a GUI program that allows for the selection of active spaces and the creation of input files for RASPT2. We will also demonstrate the computational times to evaluate the parallelization efficiencies of the CASCI-CASPT2 program for the UO_2^{2+} molecule. Furthermore, we will discuss the calculation results of the vertical excitation energies for gas-phase UO_2^{2+} molecules, along with data from several previous works for comparison. As an example of the application of actinide compounds, we will present the f-f transition excitation energies at the CASCI-CASPT2 level for the $Cm(Phen)_2(H_2O)_4^{3+}$ compound. These calculation results can explain the experimental peaks observed in Resonant Inelastic X-ray Scattering (RIXS) spectra.

[1] DIRAC: Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations. Project website: https://diracprogram.org

From crystalline solids to molecules: the incremental scheme for ab initio electron correlation energy estimates

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The incremental scheme was originally devised by H. Stoll in the 1990ies to obtain wavefunction-based ab initio calculations for correlation energies per unit cell of crystalline solids, e.g. CCSD or CCSD(T) energies for diamond or graphene. Due to the relatively small number of contributing energy increments for simple/small unit cells the calculations could be essentially carried out in a non-automated way. For general larger molecules this procedure becomes impracticable due to the lack of symmetry. Three implementations of the approach for corresponding fully automated calculations on medium-sized and large molecules [1-4] will be reviewed, with the most recent scheme reaching linear scaling of the computational effort with system size [4].

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Recent development of elongation method and its applications toward functional designs

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Quantum chemistry has been rapidly developed along with remarkable progress in recent computers, especially since the Nobel Prize in Chemistry 1981, awarded jointly to Profs. Roald Hoffmann and Kenichi Fukui on the role of frontier orbitals in chemical reactions.

On the other hand, since there is no established method to calculate the intermediate finite giant systems with random arrangement, we have been developing a linear scaling Elongation (ELG) method [1-3] as schematically shown in Figure 1 left. In this talk, I will introduce the development of the basic theory of our Elongation method, and then show its application to the functional design of NLO polymers, local excitation in large systems [4], DNA-small molecule interactions, combination with neural networks (NN) (Figure 1 right), CO_2 adsorption amine-containing polymers in multi-scale calculations, and so on.

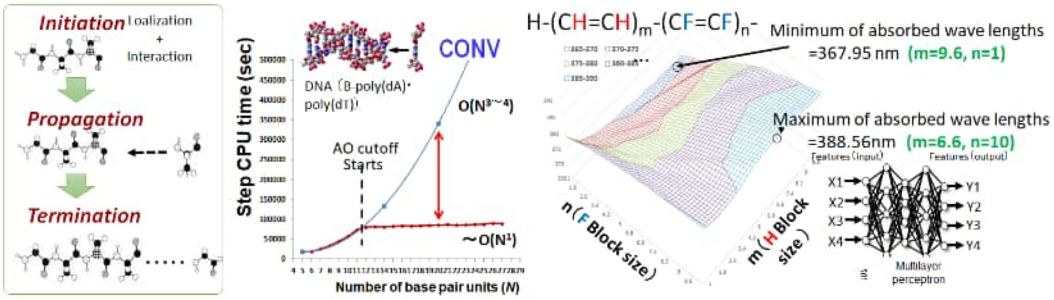

Figure 1. An example of ELG method and application to NN.

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Efficient Fragment-based Electronic Structure Methods for Excited States

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In recent years, we developed a multi-layer energy-based fragment (MLEBF) method within the many-body energy expansion framework, which supplies accurate energies and gradients and reproduces excited-state topological structures. [1-2] In addition, we also combined machine learning (ML) techniques with MLEBF, [3-5] in which the photochemically active and inert regions are separately treated with the complete active space self-consistent field (CASSCF) method and trained ML models. This QM/ML MLEBF method provides accurate energies and gradients leading to essentially same excited-state potential energy surfaces and nonadiabatic dynamics compared with full CASSCF results. Importantly, in conjunction with the use of ML models, this method exhibits a low-scaling computational cost. Finally, our work could encourage the marriage of ML with fragment-based methods to explore excited-state electronic structures and ab initio nonadiabatic dynamics of large systems.

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Transition Path Sampling studies of the evolution of reactions in enzymes

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This talk will focus on recent studies of the catalytic effect in enzymes. Our group has long used Transition Path Sampling to study the reaction and has identified dynamics within the body of the protein necessary for reaction to occur and a source of the catalytic effect. We now apply these methods to both proteins generated by laboratory evolution and by natural evolution to find how the protein dynamics is built in over the course of optimization. As a side note we study the evolutions use of quantum tunneling as a mechanism of optimization.

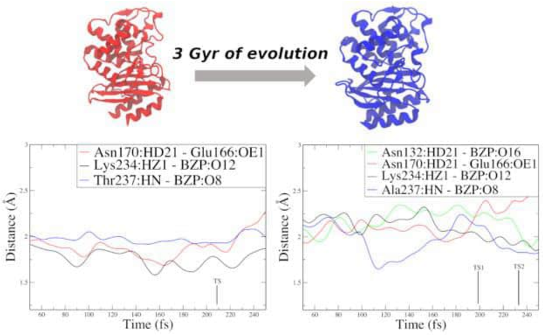

Figure. One system we study is how an ancestral β-lactamase differs in mechanistic details from a modern protein. The structures are almost identical, but there are significant mechanistic differences involving protein dynamics and electric field shaping.

Combining Resetting with Metadynamics for Improved Sampling and Kinetics Inference

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Metadynamics is a popular enhanced sampling method, whose performance relies on identifying efficient collective variables. Despite recent progress, locating collective variables that capture the slow modes of condensed phase chemical and biological process is challenging. We recently presented a collective variables-free approach to enhanced sampling using stochastic resetting [1]. We show that combining the two methods leads to greater acceleration than either approach separately [2]. We also demonstrate that resetting Metadynamics simulations performed with suboptimal collective variables can lead to speedups comparable with those obtained with optimal collective variables. Then, we show that insights from resetting inspired an improved kinetics inference scheme for infrequent Metadynamic simulations. The standard inference procedure is based on rescaling the first-passage times of the trajectories using a bias-dependent acceleration factor. While useful in many cases, it is limited to Poisson kinetics, and a reliable estimation of the unbiased rate requires slow bias deposition and prior knowledge of efficient collective variables. By limiting the inference procedure to short trajectories, experiencing minimal bias, we obtain an improved tradeoff between speedup and accuracy at no additional computational cost, especially when employing suboptimal collective variables [3].

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Identifying Most Probable Transition Path with Constant Advance Replicas

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In this talk a new constraint-based constant advance replicas (CAR) formalism will be introduced for locating the minimum energy path (MEP) and the most probable transition path (MPTP) between two given conformational states. We derive the temporal-integrated effective dynamics governing the projected subsystem under the holonomic CAR path constraints and show that a dynamical action functional can be defined and used for optimizing the MPTP. We further demonstrate how the CAR MPTP can be located by asymptotically minimizing an upper bound of the CAR action functional using a variational expectation-maximization framework. The efficiency of the proposed method will be demonstrated on the Muller potential, the alanine dipeptide isomerization, and the DNA base pairing transition (Watson-Crick to Hoogsteen) in explicit solvent.

Molecular Mechanism of Channel Transport: from Synthetic Channels to Protein

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Membrane channel proteins facilitate molecular transport across biological membranes. Inspired by these proteins, researchers have synthesized artificial channels. We investigated water transport in a pillar[5]arene channel, finding that its proton-blocking mechanism resembles natural aquaporins [1]. Positive charges at the channel entrance enhance water transport by reducing hydrogen bond lifetimes and promoting water molecule movement. Using MD simulations and Markov state models, we analyzed glycerol transport in the GlpF channel, constructing a kinetic model to predict flux under various conditions. This approach connects microscopic and macroscopic dynamics, offering a versatile tool for studying protein properties [2].

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RNA-MobiSeq: Deep mutational scanning and mobility-based selection for RNA 2D & 3D structure inference

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Tertiary structures of RNAs are increasingly found to be essential for their functions and yet are notoriously challenging to be determined by experimental techniques or predicted by energy-based and AlphaFold2-like deep-learning-based computational methods. Here, we coupled deep mutational scanning with mobility-based selection to separate structurally stable from nonstable RNA variants. The subsequent high-throughput sequencing allows the detection of the covariational signals of key secondary and tertiary base pairs with significantly improved, RNA-specific, unsupervised analysis of covariation-induced deviation of activity (CODA2) and amplification of these signals by Monte-Carlo simulated annealing. The resulting base-pairing structures can serve as the restraints for final energy-based structure predictions. This MobiSeq technique was tested on four structurally different RNAs. The results show that the detection of tertiary base pairs by MobiSeq allows reasonably accurate prediction of RNA tertiary structures. The proposed method should be useful for structural inference and improved mechanistic understanding of all RNAs with detectable changes in mobility due to deleterious mutations.

Physiological and Pharmacological Role of Protein Folding Pathways

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Over the last decade, the combined development of accurate time-resolved experimental techniques and advanced algorithms for computer simulations has opened the possibility of investigating biological mechanisms at atomic resolution with physics-based models. In particular, combination of experimental information and enhanced sampling techniques now allow the reconstruction of the co-translational folding pathways of biologically relevant proteins, at an atomic level of resolution. These innovative computational technologies reveals the existence of non-native metastable states transiently appearing along the co-transcriptional folding process of such proteins. The lifetime of these intermediates is set by the amino-acid synthesis rate, hence is in the several second time scale. In this talk, we review the evidence indicating that these protein folding intermediates play roles in post-translational regulation. We also discuss how the information encoded into protein folding pathways is being exploited in an entirely new generation of drugs capable of promoting the selective degradation of protein targets.

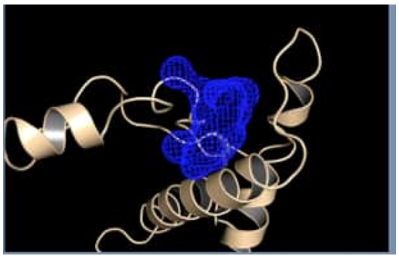

Figure 1.Druggable pocket only appearing along the protein folding pathways.

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Modeling and analyzing long-time dynamics in complex systems

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Many important physical and biochemical processes occur on time scales that are far beyond the capability of straightforward molecular dynamics simulations and are therefore called rare events. Although rare, once they occur, they can profoundly affect the function of complex molecular systems [1, 2]. Milestoning is an accurate and efficient simulation method that converts long trajectory simulations into manageable short trajectory simulations by constructing a continuous-time stochastic model. In this report, we present recent progresses on Milestoning algorithms: (i) A series of algorithms such as LPT-M, BI-M, and LiLPT-M have been developed [3], which significantly improve the accuracy and efficiency of kinetics calculations by improving the initial distribution of short trajectories; (ii) A rigorous committor function calculation method [4] and a systematic kinetic network reduction method [5] have been developed, addressing the challenges of non-Markovicity and non-reversibility in general Milestoning networks and enabling systematic reduction of kinetic network. We anticipate that the Milestoning method will be widely used in studying the long-time dynamics of complex systems.

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Multi-Scale Simulation of Photosynthesis System

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The photosynthesis process is considered the most important chemical reaction on Earth. Based on a multi-scale simulation framework, the molecular mechanisms of protein conformational variation, energy transfer, and quinol exchange in photosynthetic systems can be explored through molecular dynamics simulations, quantum chemical calculations, and enhanced sampling simulations. The report covers two aspects of the application. Firstly, by using a million-atom system model of the spinach PSII-LHCII super-complex in the membrane, microsecond-level molecular dynamics simulations were performed, with the help of the Frenkel exciton model and the master equation method, the energy transfer mechanism between the PSII-LHCII antenna and core complexes is analyzed. Secondly, based on the purple bacteria RC-LH1 complex, molecular mechanisms of quinol and quinol exchange, as well as the dissociation process of quinol molecules in the purple bacteria RC-LH1 are revealed using full-atom molecular dynamics simulations; random acceleration molecular dynamics simulations, and umbrella sampling method.

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Computational spectroscopy for precision experiments: From electroweak to quantum electrodynamical effects

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Precision spectroscopy of molecules can provide insight into nuclear structure and fundamental interactions. In this presentation, I plan to discuss the role played by parity-violating electroweak interactions in rotational spectroscopy of heavy-elemental chiral molecules, transition metal complexes [1,2] and clusters. Furthermore, I intend to highlight also recent collaborative work on the computation of nuclear magnetic resonance parameters and quantum electrodynamical corrections to these for molecules containing heavy elements [3,4].

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Quantum Chemical Calculation of ^{193}Ir Mössbauer Spectra

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^{193}Ir is a nucleus well suited for Mössbauer investigations. Conventional experiments were hampered by the need for radioactive sources, this changed with the availability of synchrotron radiation. Compared to well established methods for the calculation of, say, ^{57}Fe Mössbauer spectra, heavy elements such as iridium come with additional complications, so the toolbox for the calculation of such spectra is reviewed. This includes the proper choice of a (quasi-) relativistic Hamiltonian, how to do the picture change correction that is required if two-component methods are used, and to which extent finite nuclear size effects need be considered.

Different options have been tested against each other for a large set of iridium compounds, thus performing an internal consistency check of the theoretical methods. While Douglas-Kroll and exact quasi-relativistic (X2C) calculations give virtually the same results, picture change correction is much easier for the latter. Once the (DFT) wave function has been calculated using extended (finite) nuclei, modeling finite nuclear size in the calculation of the Mössbauer parameters has little impact. Spin-orbit coupling seems to have little effect on the calculated isomer shifts, but can be very important for quadrupole splitting, depending on the iridium oxidation state.

We compare results from calculations using the B3LYP (containing 20% exact exchange) and PBE (pure DFT) functional since they are prominent representatives for their functional class. Differences seen here are larger than those discussed above. This again tells us that the problems of relativity have largely been solved for the theoretical treatment of heavy-element chemistry, and the biggest obstacle that remains is the good old electron correlation problem.

Digital-intellectual Materials Design

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To break through the limitations of traditional material design, a new paradigm of digital-intellectual materials design has been proposed [1], covering from basic theory, material design to synthesis and application. This approach leverages the integration of data, artificial intelligence, and human expertise, not only aiming for a deep integration of experimental and theoretical methods but also emphasizing purposefulness and efficiency. It is poised to accelerate future material development. Notably, this paradigm has achieved effective carbon dioxide capture and conversion at ambient conditions, addressing the high energy consumption of traditional methods, providing theoretical and technical foundations for low-energy carbon reduction, and offering potential solutions toward carbon neutrality. [2,3]

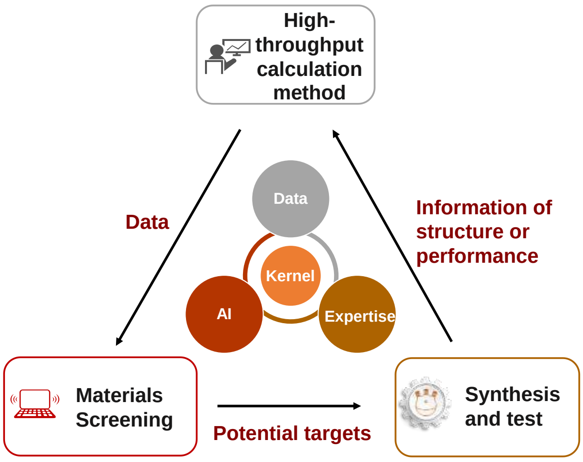

Fig. 1 Digital-Intellectual design of materials.

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Reliable predictions of crystal structures entirely from quantum mechanics

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A 1988 Nature editorial stated that one of continuing scandals in physical sciences is inability to predict crystal structures from the knowledge of the crystal monomer formula. A method developed in our group not only provides reliable predictions, but makes such predictions from first principles, i.e., not using any experimental information on the investigated systems. These predictions follow directly from quantum mechanics and can now be made for monomers consisting of a hundred or so atoms. The reasons this progress was possible are as follows. The inherent difficulty of crystal structure predictions (CSPs) stems from the fact that a given molecule can crystallize in tens of thousands plausible structures, but only a couple of them, in most cases just one, can be found experimentally. The vastness of this configuration space is due to the complexity of intermolecular interaction potentials between monomers (often called force fields, FF). The only FFs available in the 1980s and until recently were empirical FF, fitted to experimental data. It turns out that these FFs, quite successful in other applications, were not accurate enough for crystal structure predictions. *Ab initio* based FFs (aiFFs) derived from first principles using the methodology developed by our group are much more accurate and do provide reliable predictions. The main current challenge is to enable reliable predictions for flexible monomers, i.e., monomers with several soft degrees of freedom. This requires development of intramonomer aiFFs of much higher accuracy than the empirical ones. The methodology applied in CSPs can be extended to any soft condensed matter.

Chemical stabilities of OLED materials in the excited states: A DFT study

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The device lifetime of organic light emitting diodes (OLEDs) is currently of high importance and is known to be affected significantly by chemical stability of ingredient organic semiconducting molecules.[1] However, the studies regarding such molecular chemical stabilities remain in their infancy. Furthermore, theoretical studies have been limited to calculate the bond dissociation energy of molecules of interest.

In this presentation, we'll discuss about our recent results on a theoretical evaluation of not only the bond dissociation energy but also the bond dissociation rate, in particular in the excited states. This will provide a critical judgement of bond dissociation energy as a decisive parameter for molecular chemical stabilities. In addition, we'll also discuss the chemical stability from a more comprehensive perspective, considering the competition between bond dissociation and other plausible processes. [2].

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Beyond VQE methods for quantum chemistry on quantum computers

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The Variational Quantum Eigensolver (VQE) has been a prominent approach for quantum chemistry calculations on quantum computers. However, its practicality is increasingly challenged by issues such as the large number of measurement shots required to achieve accurate results. In this talk, we explore alternative methods beyond VQE for quantum chemistry calculations. This includes our recent proposal, Quantum Selected Configuration Interaction (QSCI) [1], as well as other techniques that leverage fault-tolerant quantum computing to enhance the accuracy and efficiency of chemistry calculations.

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Quantum computational chemistry

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One of the most promising suggested applications of quantum computing is solving classically intractable chemistry problems. This may help to answer unresolved questions about phenomena such as high temperature superconductivity, solid-state physics, transition metal catalysis, and certain biochemical reactions. Quantum computational chemistry is rapidly emerging as an interdisciplinary field between quantum computing and computational chemistry. This talk provides a brief introduction to major algorithms in quantum computational chemistry. After introducing the preliminaries, we review the universal algorithms with a fault-tolerant quantum computer and the variational algorithms with near-term quantum hardware for solving the electronic structure. We also discuss challenges of implementing these algorithms and opportunities of realizing quantum advantage in computational chemistry.

A general quantum algorithm for simulating open quantum dynamics

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Open quantum dynamics describes the time evolution of a system interacting with an environment and has important applications in physical chemistry, materials science, applied physics, etc. Despite its importance, there are relatively few developments of quantum algorithms for simulating open quantum dynamics, and a main challenge is to design a general quantum algorithm for physical models beyond the 2-level system and Markovian systems. To this end, we present such a general quantum algorithm based on the mathematical theory of unitary dilation. Initially demonstrated with a 2-level Markovian system (Scientific Reports, 10, 3301, 2020), this algorithm was then applied to a non-Markovian system (Physical Review Research 3, 013182, 2021). Recently, this quantum algorithm was generalized to simulating the dynamics of the Fenna-Matthews-Olson (FMO) complex (Quantum 6, 726, 2022) and the avian compass mechanism (J. Phys. Chem. Lett. 14, 3, 832, 2023), which demonstrated the ability of the algorithm to simulate the dynamics of complex biological systems.

GPU Acceleration in PySCF

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The GPU4PySCF project (https://github.com/pyscf/gpu4pyscf) integrates GPU acceleration into the PySCF package. The 1.0 release of this package features the GPU-accelerated Hartree-Fock (HF) and Density Functional Theory (DFT) calculations, along with their nuclear gradients and Hessians [1,2]. The computation of two-electron repulsion integrals (ERIs) is efficiently handled using the Rys quadrature algorithm for up to g-type Gaussian basis functions. This GPU implementation achieves a significant performance enhancement, offering a speedup ranging from 500 to 2000 times compared to traditional PySCF runs on a pure CPU setup. The project ensures full compatibility with the existing PySCF APIs, allowing users to activate GPU acceleration seamlessly using the same codebase developed for the CPU version. This package is now available on PyPI, ready for installation and use as a standard Python package. In this presentation, we will explore the design, techniques, and features available in the GPU4PySCF project.

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Target State Optimization Density Functional Theory

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Target state optimization density functional theory (TSO-DFT) is a powerful self-consistent field method for studying electronic excited and diabatic states. Its essential idea is to divide the molecular orbitals into different subspaces according to the properties of the target excited or diabatic state. In the self-consistent field optimization, orbitals belonging to different subspaces do not mix and are not orthogonal. Unlike the traditional ΔSCF method, TSO-DFT does not collapse back to the ground state, low-lying excited state or adiabatic state. The TSO method has been applied to many different types of practical chemical problems. For the valence excited states of organic compounds, the vertical excitation energies calculated by TSO-DFT and time-dependent density functional theory (TD-DFT) have similar accuracy, while TSO-DFT has a clear advantage in adiabatic excitation energies; for core electronic excitations, doubly excited states and charge transfer excited states, TSO-DFT performs significantly better than the TD-DFT method in both qualitative and quantitative results. In particular, the TSO-DFT method was used to study the relationship between the coupling and distance between the two excited states of the light-harvesting compounds in photosynthetic system II, successfully explaining the mechanism of the change in light absorption behavior observed in the experiment. In the diabatic calculation, TSO-DFT can clearly define the charge and spin of molecular fragments, which can be used for energy decomposition of the excitation or energy transfer processes. TSO-DFT has been implemented in the computational chemistry software Qbics developed by us, which can be a powerful tool for chemists.

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A molecular dynamics simulation software for polymers

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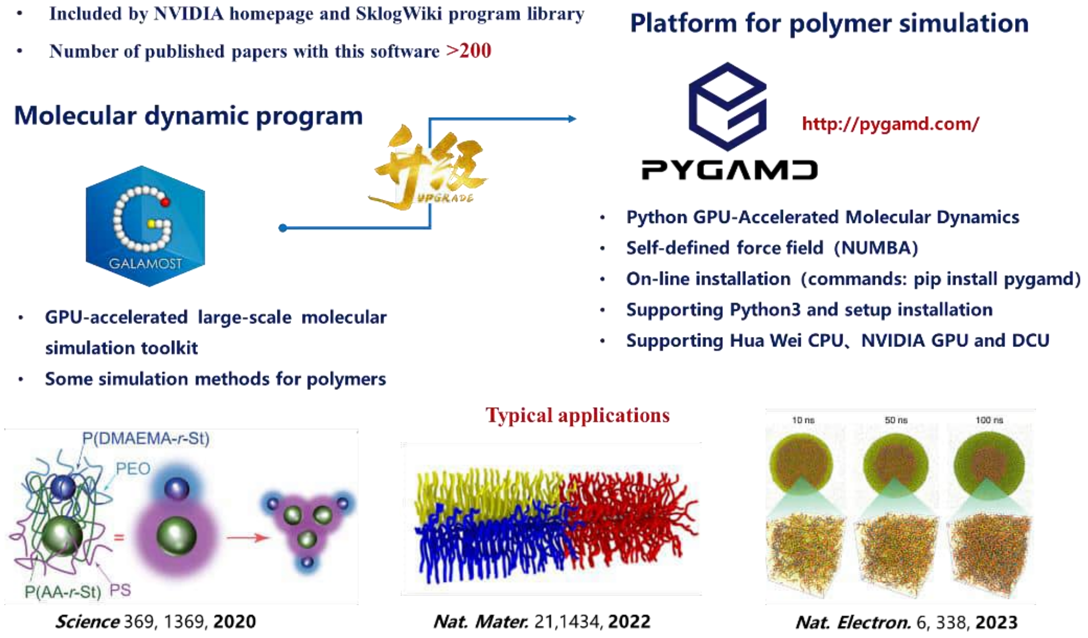
Abstract

It is a daunting challenge to simulate polymers by molecular dynamics (MD) simulations due to the large size and long relaxation time of polymer chains. Combining coarse-grained models and GPU-accelerated computation, we develop a software for the large-scale MD simulations of polymers. The name of software is PYGAMD (Python GPU-Accelerated Molecular Dynamics Software, http://pygamd.com/). It integrates modeling, dynamic simulation engine, property analysis modules with 9 innovative simulation methods. Taking dynamic bond model as an example, we show how to employ MD simulation method to reveal the mechanism of enhancing the mechanical properties of polymers by hydrogen or coordinate bond interactions.



- Included by NVIDIA homepage and SklogWiki program library
- Number of published papers with this software >200

Molecular dynamic program

- GPU-accelerated large-scale molecular simulation toolkit
- Some simulation methods for polymers

Platform for polymer simulation

http://pygamd.com/

- Python GPU-Accelerated Molecular Dynamics
- Self-defined force field（NUMBA)
- On-line installation（commands: pip install pygamd)
- Supporting Python3 and setup installation
- Supporting Hua Wei CPU、NVIDIA GPU and DCU

Typical applications

Science 369, 1369, **2020**

Nat. Mater. 21,1434, **2022**

Nat. Electron. 6, 338, **2023**

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Acknowledgement

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Improving the Accuracy of Density Functional Theory via Δ-learning and Machine-learning Exact Exchange-correlation Functional

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Abstract

Density-functional theory (DFT) is a cornerstone of modern computational chemistry. Specifically, Kohn-Sham DFT greatly reduces computational costs by focusing on the real-space electron density rather than the many-body wavefunction in a higher-dimensional space. However, the catch is that the exchange-correlation (XC) functional in Kohn-Sham equation is unknown and needs to be approximated. This leads to the errors that are too large to be predictive. We proposed and developed two approaches to address this problem, *i.e.*, Δ-learning technique to calibrate the results of conventional DFT, and machine learning (ML)-based XC functional.

As approximated XC functional leads to systematic error, a simple ML model with a little extra information will be capable for calibrating the less precise results to better counterparts. Δ-learning is thus designed to learn this error with a small amount of data. Our pioneering work back in 2003 proposed a framework, proving that as simple as a one-hidden-layer neural network, together with several molecular descriptors, is enough for calibrating DFT-level results to experimental level. Later in 2022, we replaced the time-consuming DFT calculation with a graph neural network, enabling the prediction of experimental-level heat of formation in nearly no time. Δ-learning method has also been applied to calibrate photophysical properties, open circuit voltages of lithium-ion batteries, *etc*.

Another solution to improve the accuracy of DFT is to find a better XC functional. In 2004, we refined the three hybrid parameters of B3LYP XC functional to make them depend on molecular descriptors included the number of electrons, dipole moment, quadrupole moment, kinetic energy, and spin multiplicity. The functional exhibits a remarkable alignment with experimental data. Thanks to the holographic electron density theory, in 2019, we further developed a deep-learning-based algorithm that maps quasi-local electron densities to the exact XC potential. This approach not only showed excellent performance on both the training and

validation set, but also exhibited transferability and could describe van der Waals interaction. It is shown further that this approach also gives correct dissociation behaviour where conventional DFT functional fails.

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A Data Driven Robotic AI-Chemist

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The realization of automated chemical experiments by robots unveiled the prelude of artificial intelligent laboratory. We have recently built a robotic AI-chemist system that is capable of proposing scientific hypothesis after reading/disgusting existing literature, executing a full set of experiments (synthesis, characterization, and performance testing) for multiple chemical tasks, and building predictive models based on theoretical calculations and experimental data feedback, allowing to propose new hypothesis for next optimizing iteration. Over 20 distinct models and a set of 60 instructions have been developed to facilitate the collaboration of 3 types of robotics across 39 self-developed chemical stations. Within this system, over 100 experiments are conducted daily. The scope of research encompasses various fields, including photocatalysis, functional molecules, and energy materials, resulting in a thousand-fold increase in research and development efficiency. Concurrently, more than 2000 computational tasks and 10000 entries are processed simultaneously, with the entire life cycle of samples meticulously documented. Optimization algorithms, such as Bayesian methods, are integrated to enable autonomous research, while 15 models—encompassing text, graphs, tables, and classifications—are employed in the high-throughput scientific archiving process, which provides a robust foundation of data, essential for recommending experimental workflows. With the help of computations, AI chemist has the ability to find the optimal result beyond the chemical space covered by the experiments. It means that we have created a robotic AI chemist that is capable of executing all-round chemical research with data driven intelligence. In the future, the more advanced all-round AI-Chemists equipped with scientific data intelligence may cause changes to chemical R&D.

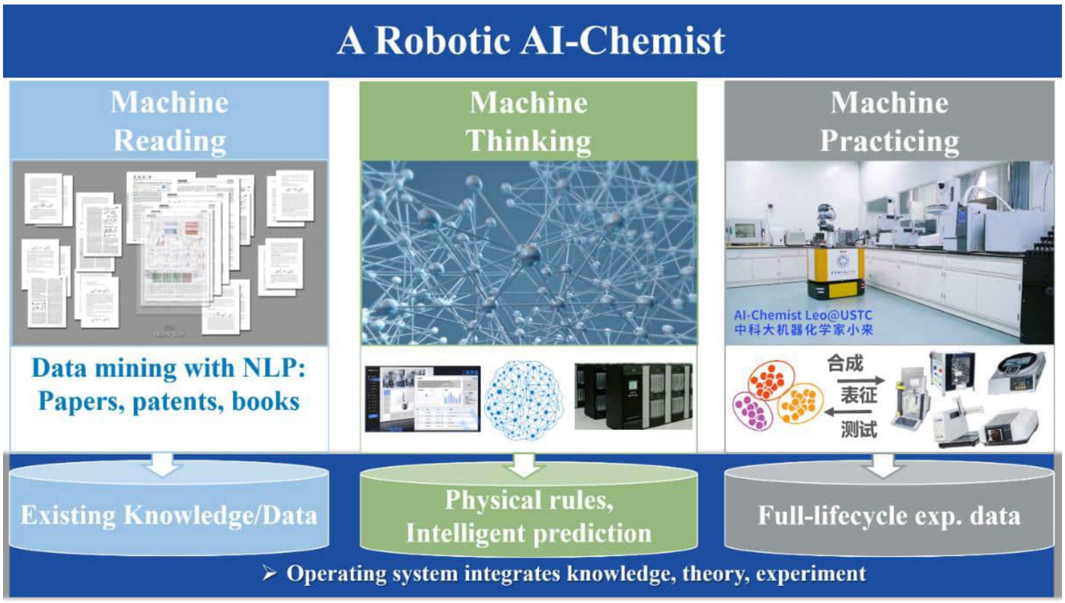

Figure 1. Three basic components of the robotic AI-Chemist system

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Active Learning for Surface Adsorption Chemistry

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Organic adsorbates at inorganic substrates play a key role in technologies ranging from catalysis to sensing. Their functionality is critically determined by the native adsorption configurations, which can be determined by simulations but often at prohibitive computational cost. Adsorbate search can be accelerated with active machine learning algorithms, where configurations are sampled on-the-fly in the search for optimal structures.

We encoded such a probabilistic algorithm into the Bayesian Optimization Structure Search (BOSS) Python tool [1]. BOSS relies on a statistical surrogate model of chemical properties to make smart decisions on sampling relevant adsorption configurations. We applied it to learn global energy landscapes and perform atomistic structure search [1] for surface adsorbates, ligand-protected clusters and thin film growth with modest dataset sizes. With recent multi-objective and multi-fidelity implementations, we can make use of different information sources to learn adsorption structures and properties at much reduced computational costs.

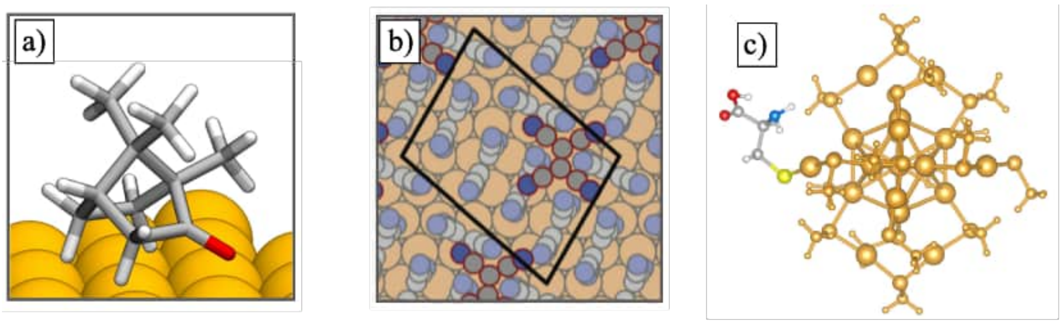

Figure 1. Active learning atomistic structure search for a) surface adsorbates, b) thin film growth and c) ligand-protected clusters.

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Green's function methods for quantum chemistry

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In this talk, I will discuss our recent developments in computational chemistry methods employing the one- and two-body Green's functions (or propagators) [1,2]. In particular, new developments around the GW approximation of the one-body propagator will be presented [3-6].

Anomalous propagators and the particle-particle channel of the Bethe-Salpeter equation formalism will also be introduced and discussed [7,8].

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Resolving shortcomings of CCSD(T) theory for metals and large molecules

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Coupled-cluster theories can be used to compute electronic correlation energies of real materials with systematically improvable accuracy. However, the widely used coupled cluster singles and doubles plus perturbative triples [CCSD(T)] method is only applicable to insulating materials. For zero-gap materials the truncation of the underlying many-body perturbation expansion leads to diverging correlation energies, also known as infrared catastrophe. We present a novel perturbative triples formalism denoted as (cT) that yields convergent correlation energies in metallic systems [1]. Furthermore, we show that this approach resolves previously reported discrepancies for interaction energies of large molecules between CCSD(T) and quantum Monte Carlo calculations [2].

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Diabatic electronic-structure theory: method development and its applications in analyzing chemical reactivity

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Abstract

In recent years, we developed several *ab initio* quantum chemistry methods to construct diabatic states with specific charge distribution characters and bonding patterns. These methods can be applied to study the chemical reactivity of several typical reactions in the diabatic representation with the evaluated diabatic properties, including electronic coupling, dipole moment etc.

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Towards efficient calculations of strongly correlated systems with Natural Orbital Functional Theory

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In this work, we present the recent advances in Piris natural orbital functionals (PNOF) as implemented in the DoNOF software,[1] which enables affordable calculations of strongly correlated systems at fourth-order scaling. The energy is an exact and known functional of the second-order reduced density matrix. PNOF harnesses this functional by providing an approximate reconstruction in terms of the natural orbitals and the occupation numbers. Furthermore, the most recent global NOF has shown good results in systems with static and dynamic correlation [2], and a recently revamped convergence scheme has allowed us to reach practical systems such as polyacenes and fullerenes. Finally, we will explore the extension of PNOF to excited-state calculations [3] and to molecular dynamics simulations [4].

Figure 1. HONO of the 12-acene computed with PNOF in DoNOF.

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TDDFT/TDHF Methods Based on Non-Orthogonal Localized Molecular Orbitals and It's Applications

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Abstract

Progress on the computational methods based on non-orthogonal localized molecular orbitals (NOLMO) is presented[1-4]. Time-dependent coupled perturbed Hartree-Fock and time-dependent DFT approaches based on non-orthogonal localized molecular orbitals (NOLMO) have been presented and used for calculating (hyper)polarizabilities of large molecules. In the presence of an external electric field, the wave function and SCF operator of an unperturbed NOLMO SCF wavefunction/orbitals are expanded to different orders of perturbations. The corresponding NOLMO-TDHF equations till the third order have been derived, which are different from those of a conventional TDHF equations because of the release of the orthogonal restrictions on molecular orbitals. The ways how to solve TDHF equations on NOLMOs are given. The program has been implemented with several chemical systems used to verify our method. This work represents the first step towards efficient calculations of molecular response and furthermore the excitation properties with NOLMOs.

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Minimally empirical double hybrids: A status update

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ABSTRACT

Minimally empirical double hybrid DFT (see [1] for a review) has emerged as an middle road between WFT and hybrid DFT that achieves accuracy near WFT at a computational cost not much greater than conventional hybrid DFT (for small and medium molecules). "Minimal empiricism" eschews the extremes of both radically empirical "quasi-machine learning" on the one hand, and nonempirical purism on the other: adjustable parameters are used sparingly and only when statistically significant beyond any doubt. The first and most widely used such functional, revDSD-PBEP86 [2], was competitive with the best double hybrid thus far, ωB97M(2) [3], but with one-third the number of adjustable parameters. Various avenues for further improvement have been explored, culminating in Refs.[4,5]. The RI-MP2 step dominates computational cost for large systems ($\gtrsim 100$ nonhydrogen atoms), but here PNO-MP2-F12 approaches [6] offer succor.

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AIDD and drug candidates by super-computing: Anti-Aging, Cancer and Covid-19

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Identifying drug-target interactions (DTIs) is an important step for drug discovery and drug repositioning(BIB 2019,2020,2021,2022). To reduce the experimental cost, many computational approaches have been developed by our team, for example, deep forest, multi-label learning and graph deep neural networks. Moreover, we updated the gold standard data set by adding 15,000 more positive DTI samples in comparison to the data set, which has widely been used by most of previously published DTI prediction methods since 2008. The proposed methods/models are applied to both data sets, demonstrating its superiority over other machine learning methods and several existing methods.

Another parallel development in designing and screening bioactive peptides against various gene targets for different diseases（Nature MI 2022）. Human leukocyte antigen (HLA) can recognize and bind foreign peptides to present them to specialized immune cells, then initiate an immune response. Computational prediction of the peptide and HLA (pHLA) binding can speed up immunogenic peptide screening and facilitate vaccine design. However, there is a lack of an automatic program to optimize mutated peptides with higher affinity to the target HLA allele. Here, to fill this gap, we develop the TransMut framework—composed of TransPHLA for pHLA binding prediction and an automatically optimized mutated peptides (AOMP) program—which can be generalized to any binding and mutation task of biomolecules. First, TransPHLA is developed by constructing a transformer-based model to predict pHLA binding, which is superior to 14 previous methods on pHLA binding prediction and neoantigen and human papilloma virus vaccine identification. For vaccine design, the AOMP program is then developed by exploiting the attention scores generated by TransPHLA to automatically optimize mutated peptides with higher affinity to the target HLA allele and with high homology to the source peptide. The proposed framework may automatically generate potential peptide vaccines for experimentalists.

In searching for drug candidates against COVID-19, we propose a new nonlinear end-to-end model called LUNAR(BIB 2022). It uses graph convolutional neural networks to automatically learn the neighborhood information of complex heterogeneous relational networks and combines the attention mechanism to reflect the importance of the sum of different types of neighbourhood information to obtain the representation characteristics of each node. These AIDD tools are used to screening drug candidates of various kinds combing structural based atomic simulations. Some promising molecules have been found. An active compound kaempferol from the Traditional Chinese Medicine (TCM) was found to be an inhibitor of the main protease. It was found that kaempferol (62.50–125.00 μg/ml, IC50 31.25 μg/ml) significantly abridged the CPE instigated by an infection in Vero E6 cells, which indicates it could be a promising SARS-CoV-2 antiviral drug.

Intestinal epithelium encounters trillions of microorganisms, including various viruses. To cope with the microbial threat, intestinal cells have evolved to produce antimicrobial peptides, including HD5(Gastroenterology 2020), which is a lectin-like peptide able to bind lipids and glycosylated proteins. In this study, we found by large scale simulations a structure-dependent interaction between HD5 and ACE2.The binding of HD5 to ACE2 cloaked several sites in the ligand-binding domain, among which Asp30and Lys31 are crucial for SARS-CoV spike to bind ACE2. Accordingly, SARS-CoV-2 S1 binding and S pseudovirions entry to enterocytes were inhibited by HD5. To our knowledge, this is the first study demonstrating the innate defense function of human intestine against SARS-CoV-2. Our finding is a reasonable explanation to the clinical phenomenon that few intestinal symptoms are observed inpatients with COVID-19. HD5 also inhibited SARS-CoV-2S pseudovirions entry to human renal proximal tubularepithelial cells, demonstrating an extensive protection of HD5. For the shortage of effective drugs to prevent and treat COVID-19, we think that it may be a useful strategy to increase the content of HD5 in vivoby oral administration. This work was recommended by Prof. Jens-Michael Schröder in Faculty Opinions: “They identified the lectin-like antimicrobial and antiviral enteric alpha-defensin HD5 as the effector molecule of the gut’s innate defense system towards SARS-CoV-2 infection. These findings may suggest a new option to prevent or treat COVID-19 either by using HD5 as a therapeutic or by stimulating endogenous HD5 synthesis”(Gastroenterology 2020).

The rare event dynamics simulations can be also be used to understand, for example antivirus drug by calculating the kinetic and thermodynamic free energy profiles on the drug binding sites in the M2 proton channel. Our results give a theoretical framework to interpret and reconcile existing and often conflicting results regarding these two binding sites, thus helping to expand our understanding of M2 drug binding, and may help guide the design and screening of novel drugs to combat the virus (JACS, 2011).

Although my research is related to AI and computation, I was able to get involved in translation medicine due to our discovery of wgx-50, a new agonist of a membrane protein, α7nAChR, which is extracted from the Sichuan pepper, a result from extensive so called network pharmacology based in AIDD. Extensive experimental studies show it could combine with α7nAChR on nerve cells, induce depolymerization of Aβ, inhibit Aβ-induced neurocyte apoptosis, and suppress the release of TNF-αand IL-1β from microglia. In vivo experiments showed that it could improve the cognition ability in APP-Transgenic Mice. These results suggest that wgx50 is a promising drug candidate for AD treatment. Anti-aging potential was explored with C. elegans and mouse model, the life span are significant increased, about 30% and 100% respectively. Mouse models were also used to evaluated the potential cardio-protective effect of wgx-50. It is found that it effectively reduces iron accumulation, preserves mitochondrial function, regulates lipid metabolism, and maintains cell redox status, thereby protecting cardiomyocytes from DOX-induced ferroptosis.

Brief Biograph

Dr. Dong-Qing Wei, FRSC, is a distinguished Professor of Bioinformatics at College of Life Science, Shanghai Jiaotong University and editor-in-chief of "Interdisciplinary Sciences-Computational Life Sciences". Over the past forty decades he has made many grand breaking contributions to the development of bioinformatics/AI drug design techniques and their interdisciplinary applications to systems of ever-increasing complexity. He is best known for contributions to the development of molecular simulation and AI tools with applications to a wide range of chemical, physical and biological systems, from electrolytes, to polar liquids, to ferroelectric liquid crystals, to combined Quantum Mechanical/Molecular Mechanical (QM/MM) systems, to membrane proteins, protein-ligand and protein-protein complexes applied to computer aided drug design. His most important contributions in sciences are exemplified by the discovery of ferroelectric nematic liquids crystals, the first complete **ab initio** MD simulation of explosion (nitromethane), and anti-aging and anti-AD drug candidate WGX-50. Prof. Wei published more than 600 papers, 11 monographs with more than 16000 SCI citations, a h-index of 69 and i10-index 330. He was invited to give invited and plenary talks in more than 100 conferences, he also organized more than 20 national/international conferences, for example, Theory and Computational Chemistry(ACC2008), 2021 National Bioinformatics Conference, AI and Precision Medicine(2017-2018)， and International Conference on Computational and System Biology(ICCSB)(2009-2015), among others.

Ab initio molecular dynamics simulation of fullerene-like and graphene-like uranyl materials

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Uranium is a common f-block actinide element in nature, playing an indispensable role in the nuclear industry, energy, military and other fields. Uranium oxide UO_2^{2+} is the most common compound composed of uranium. This work takes the topological structural similarity between U_{60} and fullerene carbon cluster C_{60} as the starting point. Through analogy analysis, it is found that the sp^2 hybrid orbital form of carbon atoms in fullerene C_{60} is similar to the coordination environment of uranyl equatorial plane in U_{60}, which further illustrates the similarity in electronic structure between uranyl and sp^2 hybridized carbon atoms. By using the latest developed actinide pseudopotential and basis set, it is theoretically predicted that the graphene-like two-dimensional uranyl material has dynamic and thermodynamic stability, and is expected to be further synthesized in the laboratory. In addition, theoretical studies have shown that there is a one-dimensional antiferromagnetic Heisenberg chain composed of superoxide (O_2^-) 2p orbitals in graphene-like two-dimensional uranyl materials. The stability mechanism of the one-dimensional antiferromagnetic Heisenberg chain can be explained by the $2p_\pi^*$–$5f_\delta$–$2p_\pi^*$ superexchange interaction model. This article expands the design of graphene-like two-dimensional materials from s-block and d-block elements to f-block actinides, enriching the research field of two-dimensional materials and promoting the potential application of 2p orbital antiferromagnetic electronic device materials.

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Long Short-Term Memory Networks for Surface Hopping Dynamics Simulations of Photochemical Reactions

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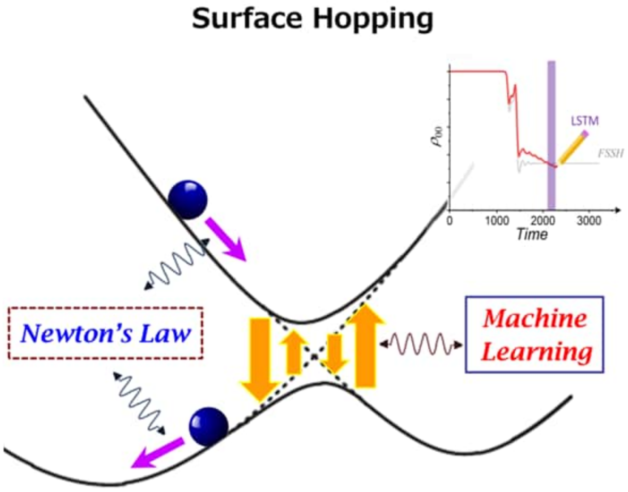
Deep learning has been proved as a powerful computational tool for nonadiabatic molecular dynamics simulations. Recently, we built long short-term memory (LSTM) networks as a machine learning-based propagator to evolve the electronic subsystem during surface hopping dynamics. Expensive calculation of nonadiabatic coupling vectors is no longer necessary. The LSTM model can be further extended from Tully’s model systems to polyatomic molecules. The construction on adiabatic potential energy surfaces with machine learning significantly accelerates dynamics simulations of photochemical reactions.



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LASSIS: a general model space recipe for two-step diagonalization of multimetallic molecular wave functions

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Spin-state energy spectra and potential energy surfaces of multimetallic complexes which are characterized by subtle magnetic interactions can be approached by the strategy of two-step diagonalization, in which the molecular Hamiltonian is diagonalized in a model space basis of tensor-product wave functions, which in turn are prototypically constructed by diagonalizing the molecular Hamiltonian projected into multiple localized fragment subspaces and retaining only a selection of low-energy fragment eigenstates. This procedure naturally raises the question of how the fragment bases are to be truncated, and what tensor product model states are to be constructed from them – in essence, a generalization of the infamous "active space selection problem." Here, we introduce a general automatic model-space selection formula for a two-step diagonalization based on a single product state reference wave function: localized active space state interaction singles (LASSIS). LASSIS is designed to qualitatively recover strong inter-fragment correlation omitted by the reference wave function efficiently and size-consistently, without requiring any user-supplied parameters. Test calculations on several multimetallic molecules show that LASSIS followed by MC-PDFT energy recalculations qualitatively recover DMRG-PDFT results, indicating that the electron correlation omitted by the approximate model space of LASSIS is primarily dynamical.

Approximating the bi-functional of the nonadditive kinetic potential for Frozen-Density Embedding Theory based multi-level simulations

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The bi-functional of the nonadditive kinetic potential is defined by means of the functional $T_s[\rho]$ (the kinetic energy in the non-interacting reference system):

$$v_T^{nad}[\rho_A,\rho_B] = \left.\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A+\rho_B} - \left.\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A}$$

It is used in multi-scale simulations of the electronic structure of species in condensed phase based on Frozen-Density Embedding Theory [1]. In this paper, we overview our work on exact relations involving $v_T^{nad}[\rho_A,\rho_B]$ and the corresponding bi-functional for energy $T_s^{nad}[\rho_A,\rho_B]$ as well as on approximating these functionals by means of an explicit analytic expression [3-6]. We will focus on emerging issues relating to the bottom-up strategy to approximate $v_T^{nad}[\rho_A,\rho_B]$ directly [4-6], i.e. without constructing the approximation for the parent functional $T_s[\rho]$.

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Relativistic Equation-of-Motion Coupled-Cluster for Single and Double Ionization

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Equation-of-motion coupled-cluster theory provides a systematically improvable framework for the reliable representation of electronic excited states in complex many-electron systems. A relativistic formulation of EOM-CC theory based on the exact two-component framework can provide a high-accuracy description of spin-free and spin-orbit relativistic effects. In this talk, I will discuss the ionization potential (IP) and double ionization potential (DIP) forms of EOM-CC and present resent results for molecular systems for which a reliable description of spin-orbit coupling is necessary.

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Pseudopotential Studies on the Complexation of Uranyl with Fluoride

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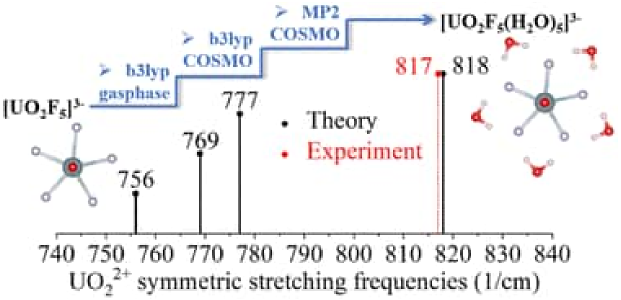
Relativistic ab initio pseudopotentials(PPs) were used combined with DFT and ab initio methods to study the complexation of uranyl with fluoride, i.e., a complete set of $[UO_2(H_2O)_mF_n]^{2-n}$ complexes (n=0-5), both for gas phase as well as for aqueous solution modelling bulk water with the conductor-like screening model. Electronic structure calculations at the Møller-Plesset second-order perturbation theory level provide accurate geometrical parameters and in particular reveal that k water molecules in the second coordination sphere coordinating to the F^- ligands in the resulting $[UO_2(H_2O)_mF_n]^{2-n}(H_2O)_k$ complexes need to be treated explicitly in order to obtain vibrational frequencies in very good agreement with experimental data. Moreover, the calculated results together with the experimental observations proved the existence of UO_2F_5 for the first time[1]. The results obtained from the large core PPs and small core PPs will be compared and discussed [2].



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[2] unpublised results

Over-destabilization vs. over-stabilization in theoretical analysis of f-orbital covalency

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The complex nature of the f-orbital electronic structures and their interaction with the chemical environment pose significant computational challenges. Advanced computational techniques that variationally include scalar relativities and spin-orbit coupling directly at the molecular orbital level have been developed to address this complexity. Among these, variational relativistic multiconfigurational multireference methods stand out for their high accuracy and systematic improvement for studies of f-block complexes [1]. Additionally, these advanced methods offer the potential for calibrating low-scaling electronic structure methods such as density functional theory. However, studies on the Cl K-edge x-ray absorption spectra of the $Ce(III)Cl_6^{3-}$ and $Ce(IV)Cl_6^{2-}$ complexes show that time-dependent density functional theory with approximate exchange-correlation kernels can lead to inaccuracies, resulting in an over-stabilization of 4f orbitals and incorrect assessments of covalency [2]. In contrast, approaches utilizing small active space wave function methods may understate the stability of these orbitals. The results herein demonstrate the need for large active space, multireference, variational relativistic methods in studying f-block complexes.

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

Krzysztof Szalewicz
University of Delaware

Bogumił Jeziorski passed away on 15th of September 2023. He was a giant figure in theory of intermolecular forces. This lecture will highlight his key novel insights in this field as well as in broader field of theoretical chemistry.

Remembering Professor Josef Paldus: Pioneer of Modern Electronic Structure Theory and Caring Mentor, Educator, and Friend

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On January 15th, 2023, our community lost an extraordinary person, a legendary scientist, and a cherished friend to many: Professor Josef Paldus. A towering figure in the history of theoretical chemistry and chemical physics, Professor Paldus is widely acclaimed for his groundbreaking contributions to the quantum theory of many-electron systems. Especially important are his seminal work on the exploitation of dynamical symmetries and Lie-group algebraic techniques in examining the many-electron correlation problem, which resulted in the development of the unitary group approach, revolutionizing configuration interaction computations, and his introduction, with his friend and collaborator of many years, Professor Jiří Čížek, of the quantum-field-theory-inspired diagrammatic methods and coupled-cluster theory, which is nowadays regarded as a gold standard of quantum chemistry, to the forefront molecular science. Similarly influential is his work, also with Professor Čížek, on the stability conditions of Hartree–Fock equations and the significance of broken-symmetry independent-particle models in studies of strongly correlated systems. His numerous contributions to areas ranging from the multireference, externally corrected, time-dependent, linear-response, and spin-adapted coupled-cluster methods to the many-body perturbation theory, approximate coupled-pair approaches, Green’s function techniques, valence-bond theory, geminals, and rovibrational and electronic spectroscopies, which he discussed in about 330 publications and countless invited lectures and conference presentations worldwide, stand as a hall of fame in molecular quantum mechanics.

In this lecture, we will embark on a journey to honor the life and work of Professor Paldus. Many of us, including the presenter, have lost a cherished friend, collaborator, and mentor. This lecture is the presenter‘s humble tribute to Professor Paldus’s exceptional life, contributions, and enduring impact on molecular science. Professor Paldus, whom many of us affectionately called “Joe”, will always be remembered for his pioneering role in modern electronic structure theory, his passionate dedication to scientific inquiry, and, above all, his humanity. In his passing, we lost not only a great visionary whose work has inspired and will continue to inspire generations, but also a kind and modest human being, a wonderful mentor and educator, a caring family man, and friend to all.

Remembering Professor Auchin Tang: Pioneer and Founder of Modern Theoretical Chemistry in China and Outstanding Educator

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Auchin Tang (1915-2008) was a renowned theoretical chemist and an outstanding educator from China. Tang was the president of Jilin University, and the first director of the National Natural Science Foundation of China. In 1955, he was elected a member of the Chinese Academy of Sciences. Tang received the National Natural Science Award five times, including twice receiving the First Prize.

In the 1950s, Tang studied the theory of chemical bonding functions and intramolecular rotation. He proposed a potential energy function formula that could be used to calculate the energy change of complex intramolecular rotations, and used molecular mechanics to calculate molecular conformations. In the 1960s, Tang established a set of incommensurable tensor methods from continuous groups to point groups, thus unifying various schemes of collocation field theory. In the 1970s, Tang focused on the study of molecular orbital graph theory and proposed three graph theorems that simplified quantum chemical calculations for homologs, molecules, and compounds with repeating units. In the 1980s, Tang proposed structural rules for atomic clusters that are more widely applicable than Wade's rules. In the 1990s, Tang conducted theoretical research on high-carbon atomic clusters and predicted the existence of a highly symmetrical and stable fullerene compound.

Tang has successively hosted twelve famous theoretical chemistry seminars, and has trained a number of Chinese theoretical chemistry research teams of international standard. Among them, Tang's ‘eight disciples’ are the most famous, and these ‘eight disciples’ have all become well-known chemists. Tang has practiced the scientific research spirit of ‘dedication, truth-seeking, innovation and collaboration’ throughout his life. His motivation for his work stems from his deep love for pursuing truth in natural sciences, as well as his strong sense of responsibility for nurturing scientific and technological talents.

Professor Tang is a true master. Remember him forever!

Highly Coarse-grained Patchy Ellipsoid Particle Model of Glucose

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Glycan chains are widely present in living organisms, with specific glycan structures encoding vital biological functions. However, the structural diversity and conformational variability of glycans present significant challenges in linking molecular properties to functional outcomes [1]. To address these challenges and enable larger-scale simulations, coarse-graining of molecules is a widely adopted strategy. The Martini force field, through extensive parameter optimization for carbohydrates, accurately captures their conformational properties and some functional characteristics. However, simulations for high-concentration monosaccharide solutions at large spatial scales still require higher coarse-graining level model [2]. This study proposes a novel coarse-graining scheme for glucose molecules, simplifying them into patchy ellipsoid particles and fitting non-bonded interactions using the Gay-Berne (GB) potential [3]. By constructing glucose dimer models with various glycosidic linkages and performing flexible scans of bond lengths, bond angles, and dihedral angles using the M062X/6-31g(d,p) method, harmonic functions were fitted to determine the corresponding spring constants, equilibrium bond lengths, and bond angles. Additionally, dihedral potential terms were obtained through decoupling and averaging systematic calculations. This scheme holds promise for high-quality simulations of larger-scale glycolipid or glycoprotein systems.

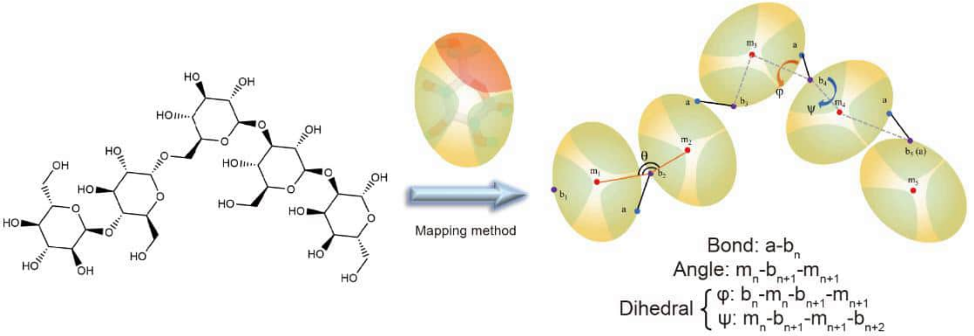

Figure 1. Coarse-grained mapping of glucose oligosaccharides to patchy ellipsoid particles. Each glucose molecule is simplified into a patchy ellipsoid, with the ellipsoid and patch sizes based on the molecule's dimensions and local features. In this model, the C1 and C2 atoms with their hydroxyl groups, the C3 and C4 atoms, and the C5 and C6 atoms are grouped into distinct patches (light green and orange-red). In this model, point m (red) represents the ellipsoid's center of mass, point a (blue) indicates the reactive site linked to the C1 atom, and point b (purple) marks the polymerization site for glycosidic bond formation. The cartoon also specifies the locations and angles of bonds, bond angles, and dihedral angles.

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Atomistic Insights on Recognition of Transcription Factor Binding Motif in DNA through bZIP Domain

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Sequence-specific recognition of transcription factor (TF) binding motifs in the target site of DNA over the vast amount of non-target DNA is vital for the transcriptional regulations of gene expression. It is primary important to characterize the preferred binding motifs of TFs belonging to diverse TF families and their mode of interactions. Our previous findings on sequence dependent structural features of biologically relevant short TF binding DNA motifs indicate the potential role of DNA shape features in motif recognition and TF binding. It was reported that pioneer TFs often interact with other TFs through DNA co-binding and migrant TFs only bind to a subset of their target sites, even in accessible DNA. However, settler TFs always bind to sites matching their DNA-binding motif not in inaccessible DNA sites. Thus, TF-DNA interaction may rely on the unique motif environment, specific to each TF. Little is known about how DNA motif environment and DNA shape features can influence the target search mechanism and sequence specific binding of different TFs to control their gene regulatory functions. Our atomistic molecular simulation studies on DNA binding motif of TFs AP-1, binding mode and interaction of human AP-1 FosB/JunD bZIP domain with DNA illustrate the role of DNA shape features, selective base specific interactions, ion binding and solvation properties of the DNA grooves to form motif sequence specific AP-1-DNA complex. We addressed the role of intrinsic motion of bZIP domain of AP-1 factors in terms of opening and closing gripper motions of DNA binding helices, in target site recognition and binding with DNA. Systematic closing gripper motion of bZIP domain is found to associate with the adjustment of helical twist of DNA, which can be important for the regulation of DNA supercoiling transitions and, by extension, transcriptional control. Our observations also suggest that binding to the cognate motif in DNA is mainly accompanied with the structural deformation of DNA to form base specific interactions, and precise adjustment of closing gripper motion of DNA binding helices of bZIP domain. As bZIP domain of AP-1 possesses unique DNA binding feature among all the species, the mode of the protein–DNA recognition can be universal for bZIP factors. Overall, this study expected to provide more insight about the target search and structure-based mechanisms of AP-1 TFs-DNA interaction.

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Structure and Catalytic Properties of Cu-Au Nanoparticles under High CO and O Coverage

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Copper-gold nanoparticles have attracted interest as catalysts for CO_2 reduction and CO oxidation due to their corrosion resistance, lower cost, and the ability to control catalytic properties. These reactions may involve substantial amounts of CO and O adsorbed on the catalyst surface, which affects both the structural properties of the catalyst and the reaction kinetics. In this study, we used density functional theory (DFT) calculations combined with machine learning methods (MLIP) to examine the changes in adsorption energy at high CO_n and O_n coverage ($1 \leq n \leq 75$) and the effect of metal ratios on the catalytic properties of 1.1 nm CuAu nanoparticles. Copper-rich compositions were found to be more favorable for adsorption, while gold-rich configurations showed lower efficiency. The adsorption patterns of CO and O in different Cu-Au compositions demonstrate similarities. It was established that a high CO content in the reaction environment increases the mobility of transition metal atoms, leading to cluster deformation. In contrast, the adsorption of O atoms results in a reconstruction of the Cu-Au coordination and encapsulation into the inner cavity. Configurations with a moderate copper content on the surface can mediate the competitive adsorption of CO and O, making such compositions promising catalysts for both oxidation and minimizing CO poisoning.

This work was supported by the Russian Science Foundation (Grant No. 19-72-30043).

Computational screening of doped-$V_3C_2O_2$ for propane dehydrogenation using DFT-based microkinetic simulations

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Propylene plays a crucial role in petrochemical industry, serving as a feedstock for various chemical compounds [1]. Abundant and cost-effective shale gas has influenced propane dehydrogenation (PDH) for obtaining propylene [2]. Herein, the impact of dopants (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) in $V_3C_2O_2$ is investigated by DFT based microkinetic simulations for PDH reaction. The d-band center of the dopant approaching Fermi level exhibits greater propane adsorption tendency, and their associated electronegativity directly impacts first C-H bond activation, serving as the activity descriptor. Overall, Cr doped $V_3C_2O_2$ offers ~2.5 fold higher catalytic activity than pristine $V_3C_2O_2$. Downshifting of apparent activation energy with increasing temperature facilitates C_3H_8 conversion (~7.3 site^{-1}sec^{-1}) and C_3H_6 TOF (~1.4 sec^{-1}) at 800 K. Primary-to-secondary hydrogen abstraction is the main reaction pathway as revealed by reactant flux analysis.

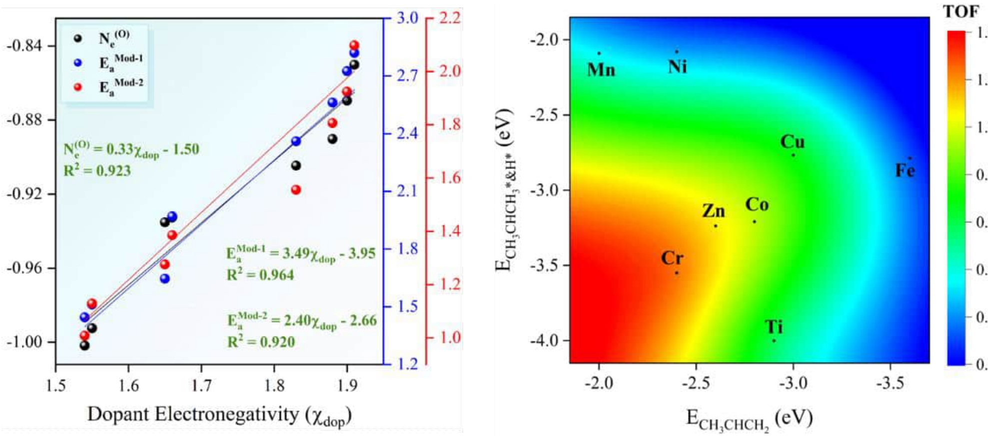

Figure 1. Correlation between (a) C-H bond activation and dopant's electronegativity, (b) TOF, iso-propyl & H and propylene adsorption

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Modeling Realistic Structures of Trimetallic Nanoalloy Catalysts Using Chemically Meaningful Descriptors

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The computational design of alloy catalysts is hindered by the uncertainty in their structure and arrangement of constituent elements within the lattice of catalyst particles, i.e., their chemical ordering. [1] Moreover, chemical ordering in alloy nanoparticles (nanoalloys) can be affected by the reaction temperature due to thermal disorder. In this study, we develop a method for realistic simulations of trimetallic alloy nanocrystallites with the lowest energy chemical ordering or chemical ordering taking into account thermal disorder in the nanoalloy. This method is based on Monte Carlo simulations using topological lattice Hamiltonian, whose parameters are fitted to the results of density functional (DFT) simulations of thoughtfully designed archetypal nanoalloy structures. The implementation of this method in Python code is freely available online. [2] Using this method, we characterized chemical orderings in nanoparticles composed of 79 and 338 atoms of metals with known catalytic activity in CO_2 hydrogenation, namely, Pd-Pt-Cu, Ni-Pd-Cu, and Co-Rh-Cu (Figure 1). Our simulations show that the thermal disorder in these alloys significantly affects the composition of surface sites. Such structural changes are demonstrated to affect the average binding energies of reaction intermediates to the catalyst surface by up to 1.1 eV, implying their critical effect on the alloy’s catalytic properties. Moreover, we demonstrate how the developed code can be used for brute-force evaluation of entropic contributions to mixing free energies in alloy nanoparticles. The demonstrated abilities of the proposed method to generate realistic models of trimetallic nanoalloys in a computationally efficient manner enable reliable simulations of catalytic properties of trimetallic catalysts for their in-depth understanding and computational design.

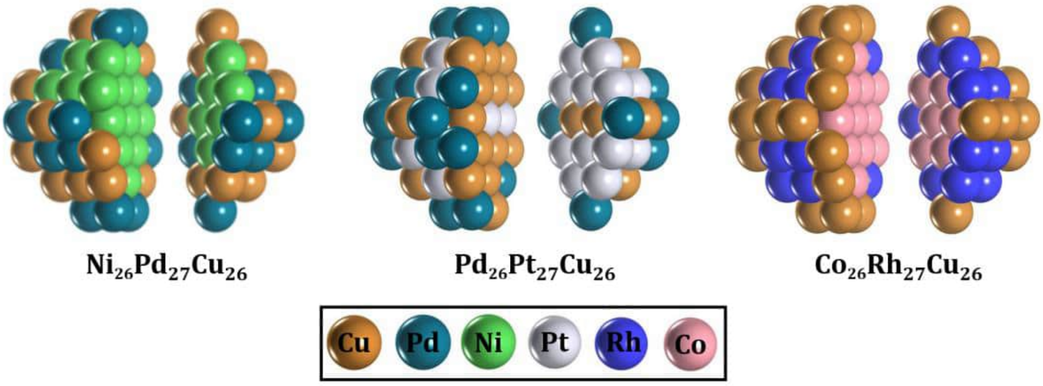
$Ni_{26}Pd_{27}Cu_{26}$ $Pd_{26}Pt_{27}Cu_{26}$ $Co_{26}Rh_{27}Cu_{26}$

Figure 1 – Lowest energy structures of 79-atom truncated octahedral Ni-Pd-Cu, Pd-Pt-Cu and Co-Rh-Cu trimetallic nanoparticles.

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Accurate Adsorption Energy Predictions Using Many-Body Methods with Quantum Embedding

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Adsorption energy plays is the pivot in surface chemistry and heterogeneous catalysis. While density functional theory (DFT) with the generalized gradient approximation (GGA) has been widely used for surface adsorption studies, it often falls short in quantitatively predicting adsorption energies and can even lead to qualitative errors, such as the well-known CO puzzle on transition metal surfaces like Cu(111), Pt(111) and others, where GGA-DFT and even hybrid DFT will misidentify the most stable adsorption site [1-2]. Conversely, wavefunction theories offer a reliable and systematically improvable alternative to DFT. But the high computational cost of wavefunction methods hinders their extensive application in accurately evaluating adsorption energy. In this work, we employ a quantum embedding approach [3-5] that partitions the surface into an active space and an environment centered around the adsorption site. High-level wavefunction methods are employed to handle the active space, which is more relevant to adsorption, while mean-field methods are used for the remaining parts to achieve a balance between accuracy and efficiency. We anticipate that this approach will offer new insights into heterogeneous catalysis and other complex interfacial problems.

Keywords*：*Adsorptions on Surface, Many-body Method, Quantum Embedding

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Illuminating tandem reactions characterized by temporal separation of catalytic activities via DFT calculations: a case study of Ni-catalyzed alkyne semihydrogenation

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The concept of “temporal separation of catalytic activities” outlines a scenario where multiple transformations within a catalytic tandem reaction proceed sequentially over time without mutual interference.[1] After presenting several examples of such reactions,[2-3] we specifically focus on an example of the Ni-catalyzed alkyne semihydrogenation as a significant case study.[4] By performing DFT calculations, we illuminate the unique dynamic character of the reaction that the intermediate remains dormant until the reactant exhausted. The insights gained from the present calculations have led us to propose a comprehensive energy landscape model for the catalytic tandem reactions with temporal separation of catalytic activities, which offers a logical explanation for the temporal dormancy of the intermediate. This class of reactions is expected to be highly valuable as it presents the opportunity to fine-tune individual reaction steps, thereby introducing fresh concepts for precise control of reactions in one-pot chemistry.

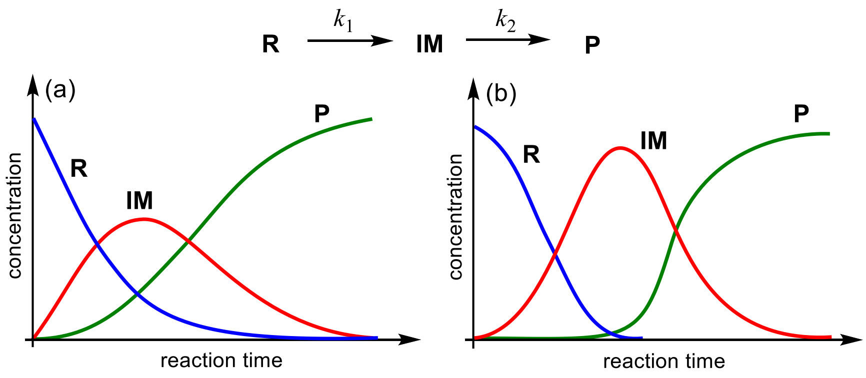

Figure 1. Conventional (a) vs. catalytic-activity temporally separated (b) two-stage catalytic tandem reaction

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Effect of ZnO Support and Nanostructuring on Catalytic Activity of Noble Metals: Insights from Sabatier Principle

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The hydrogen economy is positioned to play a significant role in mitigating carbon dioxide emissions in the coming years. One prevalent method utilized for hydrogen production involves the dehydrogenation of methane, which generates the lowest CO_2 emissions per H_2 molecule.[1] Nickel remains the commonly employed catalyst for methane reforming despite relatively low yield, which is offset by its lower cost compared to metals such as ruthenium, rhodium, or iridium.[2] The nanostructuring and the introduction of a substrate to support these metal particles are two factors that can enhance the catalytic activity of the metals. With this idea in mind, utilizing ZnO to support metal nanoparticles (NPs) has been proposed for steam reforming processes involving methanol and methane. This study investigates the effect of ZnO ($10\bar{1}0$) on metal nanoparticles of Ag, Cu, Au, Pd, Pt, and Ir and their activity in the methane reforming reaction. To achieve a realistic model, a metal NP of ~1.5 nm is suggested due to the presence of metal atoms with coordination environments like those observed in larger NPs in experimentally prepared catalysts. Then, the potential energy surface of transition metal nanoparticles on ZnO surface is studied using modern empirical potentials and density functional theory (DFT) calculations. We analyzed adsorption of relevant adsorbates in methane reforming reaction on all the non-equivalent positions of the supported NPs. Even with the presence of ZnO the scaling linear relations between adsorption energies of C vs CH_x and O vs OH are maintained. According to Sabatier principle, O and C adsorption energies determine the turnover frequency in the methane steam reforming.[3] The NP-ZnO interface exhibits the most significant increase in the adsorption energy of O and OH compared to M(111) slab. Based on the Sabatier volcano plot for the methane steam reforming reaction, such changes in the adsorption energy of O and OH suggest a significant increase in the catalytic activity of metals like Au, Cu and Ag in the reaction (Figure 1).

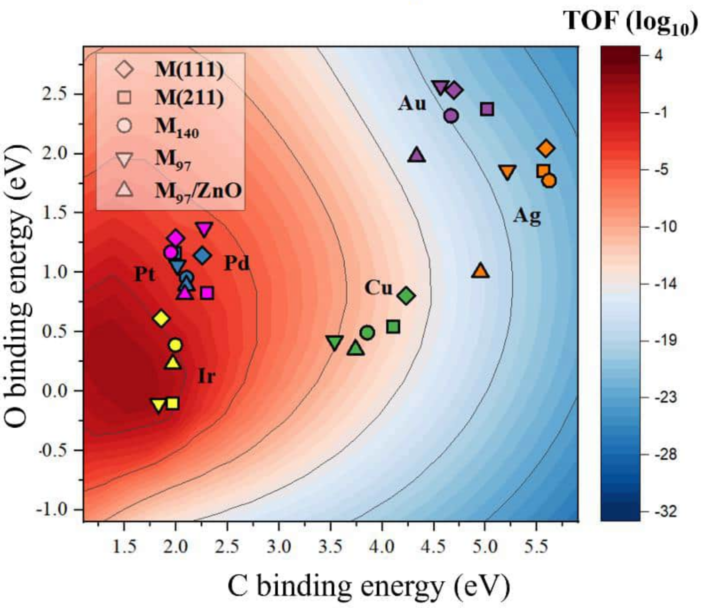

Figure 1. Volcano plot with the TOF of methane steam reforming as a function of O and C binding energies. The temperature for the microkinetic simulation is 1000 K, the pressure is 5 bar, and the conversion rate is 1%.

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Theoretical insights into the ammonia and hydrogen-induced structural evolution of Pt clusters in mordenite

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Metal/zeolite is an outstanding heterogeneous catalyst[1] in which the structure and size of metal species determines the reaction pathways. The reaction atmospheres have critical effects on the structural evolution of active metal in zeolites,[2] but its mechanism remains elusive.[3] In this work, we investigated the structure evolution of Pt_n clusters in mordenite zeolitic models to unravel the mechanism of H_2 and NH_3 atmospheres in shaping the cluster structures.

Using periodic density functional theory calculations and *ab initio* thermodynamics, the stable configurations of $Pt_n(H)_x$ and $Pt_n(NH_3)_m$ clusters are systematically compared both in gas phase and zeolite channel. Our work investigated the structure evolution of Pt_n clusters in mordenite to unravel the mechanism of H_2 and NH_3 atmospheres in shaping the Pt cluster structures. Our finding indicates that H acts as a double-edged sword, it penetrates the Pt-Pt bonds and weakens the Pt-Pt bond, but serves as a bridge that tightly links the dispersed Pt atoms. As a result, large Pt clusters (up to $Pt_7(H)_{28}$), are stable in both gas phase and zeolite channels. In contrast, NH_3 breaks the Pt-Pt bond and cannot link the dispersed units, resulting in clusters with smaller sizes, particularly the special stability of $Pt(NH_3)_2$ species. Furthermore, NH_3 binding to Pt_n significantly increases the steric size of $Pt_n(NH_3)_m$ and the formation of larger clusters are prohibited by the confinement effect. We also precisely gauge the Lewis acidity of Pt_n clusters within zeolite by considering the stepwise desorption of multiple NH_3 molecules and observe a strong relationship between the Lewis acidity, capacity and size, location of Pt_n in zeolite. These atomistic insights enhance understanding of the metal/zeolite system and establish a solid theoretical foundation for catalyst design.

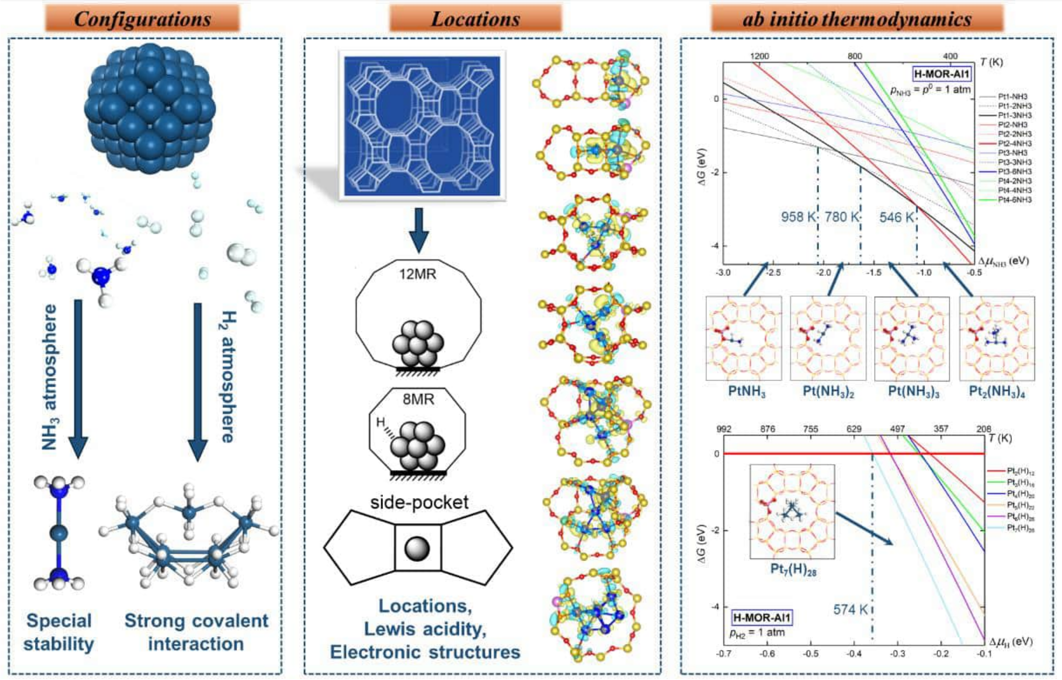

Figure 1. The process for investigating the impact of NH_3 and H_2 on the structural evolution of Pt_n clusters in mordenite.

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Mean-field QM/MM simulations for electrochemical interfaces

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Electrochemistry, the fundamental basis of sustainable energy conversion technologies, investigates the electric-chemical energy interconversion process at the electrode-electrolyte interface, where a characteristic liquid structure, namely an electric double layer (EDL) is known to be formed. Since the early 1900s, unremitting efforts have been made to identify potential-dependent EDL structural changes, but only a few molecular details have been disclosed to date. To accurately model the electrified interface, we develop a first-principles-based multiscale method called a density functional theory in classical explicit solvents (DFT-CES), which mean-field couples the DFT and the molecular dynamics for respective description of electrode and electrolyte [1]. Using DFT-CES, we find unprecedented liquid structural changes and phase transitions of the EDL [2]. Atom-level investigation on the EDL region, enabled by our DFT-CES simulations, further unravels a new mechanistic role of the cations in the EDL during CO_2 electroreduction [3]. Our studies envisage a new perspective for developing better electrocatalysts by tailoring the electrochemical interface.

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Structure-driven tuning of adsorption properties of core-shell nanoparticles: a density functional theory study

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Nanoparticles are fascinating nanoobjects that are actively studied and widely employed in various fields, such as heterogeneous catalysis and advanced electrode materials. Their local atomic structure and composition can significantly impact their properties. We employed the state-of-the-art first-principles calculations to investigate the effects of AuCu, AuPd, IrPd, IrPt nanoparticles structure and composition on the electronic properties, charge distribution, and CO and O adsorption energies. Two types of nanoparticles were examined in this study; specifically, core-shell nanoparticles and bimetallic alloy particles. Adjusting the core-to-shell ratio allows one to precisely tune the O and CO adsorption energies on the nanoparticle surface. This results in a narrower range of adsorption energies, specifically for CO adsorption, which cannot be achieved in bimetallic alloys. Our study shows the significance of this approach for fine-tuning adsorption energies on a nanoparticle surface. These results were published in Nanoscale 2024, PRB 2023, PCCP 2023, Aggregate 2022.

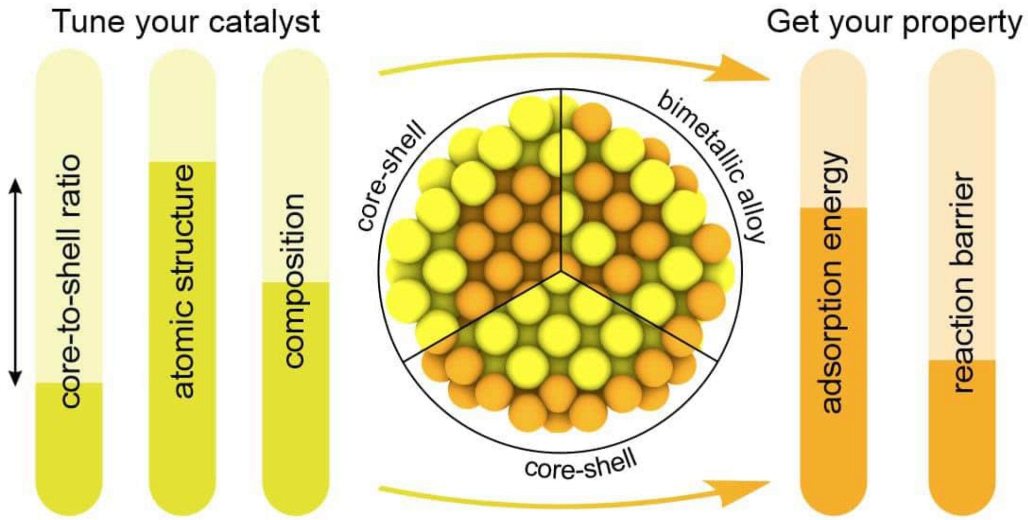

Figure 1. Scheme of tuning nanoparticle properties.

Controlling active phase and interface interactions in bimetallic Ru-Pd catalyst via CO oxidation

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Abstract: The structural and compositional changes between various active phases in heterogeneous catalysts during ambient-pressure and high-pressure reactions are notoriously challenging to investigate, which complicates the understanding and development of new catalysts. Herein, we show how the transitions between various active phases of RuPd catalysts during CO oxidation reaction affect the catalytic activity and Ru-Pd interactions using operando transmission electron microscopy (TEM) and density functional (DFT) calculations. Namely, we observed transformations from Ru nanoparticles (NPs) supported on Pd and Ru-Pd solid solutions alloys into RuO_x NPs supported on Pd at the onset of CO oxidation under O_2-rich environment and the formation of Pd@Ru core-shell NPs under CO-rich environment. Furthermore, we find that metal-oxide interactions in RuO_2/Pd NPs make this catalyst highly active at low temperatures with a prolonged lifetime; contrarily, the interactions between Pd and metallic Ru stabilize Ru against oxidation but make it more prone to CO poisoning. Thus, our results reveal how the interactions between catalyst components can be affected by the reaction conditions and may lead to puzzling changes in the catalytic activity.

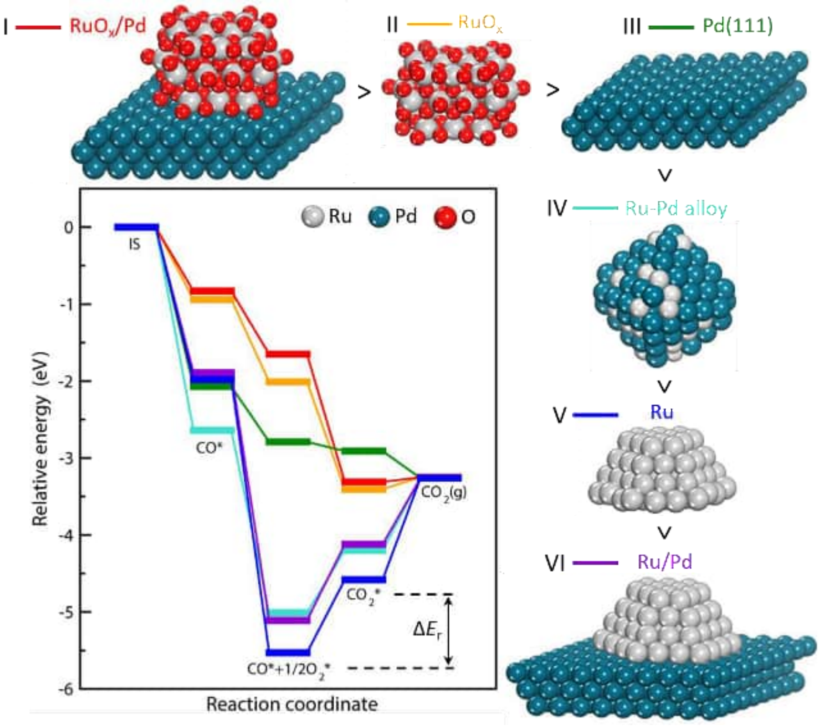

Figure 1. The structure of various morphology of Pd-Ru catalyst and energy landscape of the CO oxidation reaction.

Talk No.

Delayed Fluorescence from Inverted Singlet and Triplet Excited States in Heptazine Analogues HzT-FEX2 Studied by Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT)

Alireza Lashkaripour,† and Cheol Ho Choi*,†

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This study explores the photophysical properties of heptazine analogues, with a focus on HzT-FEX2, utilizing Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT). Heptazine derivatives are highly regarded for their exceptional stability and electronic properties, making them promising candidates for optoelectronic and photovoltaic applications. A deep understanding of the mechanisms behind their delayed fluorescence is essential for enhancing their performance in these fields. Our investigation into the singlet-triplet energy gap in heptazine analogues revealed that traditional methods using TDDFT like BHHLYP and B3LYP tend to overestimate this gap. In contrast, MRSF-TDDFT has proven to be a more efficient and accurate approach for studying these systems. To achieve optimal results, we also attempted to optimize the VAEE functional using MRSF-TDDFT.

Advances in Q-Chem 6.2

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The Q-Chem software package continues to provide a comprehensive library of cutting-edge methods for electronic structure modeling, allowing fast, accurate simulations of structures, reactivities, and properties. Our "open teamware" approach, alongside our modular developer environment, provides researchers with a well-tested foundation of code on which to develop new methods, fostering scientific collaboration and innovation while also ensuring long-term sustainability and maintenance of the developed code. This poster will discuss several recent developments from Q-Chem developer groups across the globe, including new methods for modeling X-ray spectroscopy[1], energy and force decomposition analysis, real-time nuclear-electronic orbital (NEO) methods[2], and many other new improvements.

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Extension of the charge stabilization method beyond energies

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The charge stabilization and extrapolation method [1] has been used before to obtain energies of metastable anionic states. We present an extension of this method for obtaining spatial functions for these states. The usefulness of this development is illustrated by applications to chlorinated ethene derivatives and perfluorinated cage molecules. The considered ethene derivatives form unbound anions and are subject to dissociative electron attachment (DEA). Applying charge stabilization enables detection and description of multiple unbound anionic states, and the novel use of extrapolated electron localization functions (ELFs) [2] together with Berlin's binding function [3] allows for prediction of when and where DEA will occur.[4] The studied cage molecules are hypothesized to catch an electron in the cage interior, resulting in correlation-bound anions.[5] We assessed Hartree-Fock theory and three density functionals for the characterization of the anionic states, by means of electronic Fukui functions and ELFs. Whenever the used level of theory described the anion as unbound, charge stabilization had to be employed to obtain extrapolated functions. Evidence for an electron inside the cage was found for only perfluoroadamantane, and only at optimized neutral geometry with methods that describe the anion as bound.[6]

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Noncollinear functionals for Real-time TDDFT and Gradients of Spin-flip TDDFT

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Recently, we proposed the multicollinear approach that generalizes collinear functionals to noncollinear ones. It has been applied in DFT (density functional theory)[1] and linear-response TDDFT (time-dependent density functional theory)[2] calculations. In this poster, we applied it on real-time TDDFT and linear-response spin-flip TDDFT gradients. The former is used to simulate electronic absorption spectra, Rabi resonance, and the precession of a two-magnetic center system. Thanks to the non-zero exchange-correlation torque provided by multicollinear functionals, the contributions of the local torque to spin dynamics are allowed to explore. The latter is implemented by solving a Z-vector equation with its formula being re-derived, and serves for performing optimization of spin-flip excited states.

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Unraveling the mechanism of a switchable acid catalyzed COT oxide contraction towards homoallylic alcohols

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The synthesis of 7-membered rings poses a challenge due to the limited number of reactions available. [1-3] In this context, Brønsted acid organocatalysis can be used to promote the ring contraction of cyclooctatetraene oxide towards the synthesis of 7 and 6-membered ring aldehydes that could further be activated by the same catalyst towards the enantioselective formation of homoallylic alcohols. (see Fig. 1). In this work, the 7 to 6 switchable character of this mechanism will be explored in detail, and the crucial factor of the organocatalyst's acidity on the mechanism will be revealed.

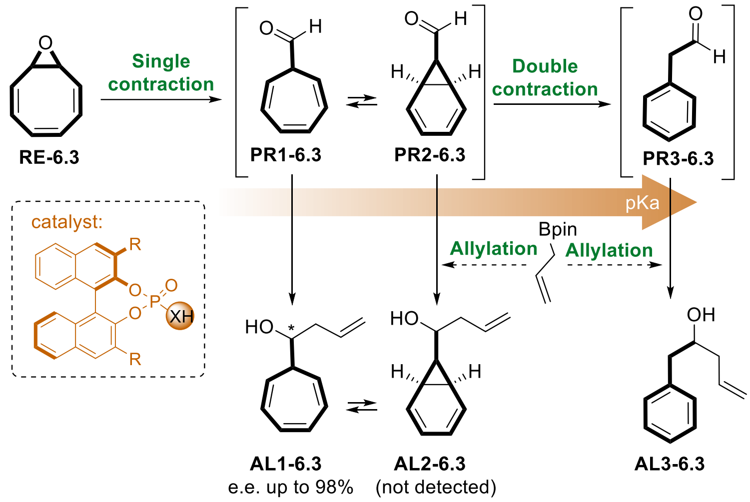

Figure 1. Single and double ring contraction coupled with the enantioselective allylation

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Some Restrictive Open-Shell Excited-State ΔSCF Methods

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Accurate calculation of excited states is crucial in the field of chemistry, but the current mainstream method for computing excited states, TDDFT, still lacks accuracy in certain aspects. To improve precision while keeping computational demands comparable to TDDFT, the projection △SCF method and associated programs have been developed, including: unrestricted Hartree-Fock (UHF); constrained unrestricted Hartree-Fock (CUHF); spin-flip restricted open-shell (SFRO), which uses triplet excited states with Ms=1 for spin-flip to achieve mixed states; and restricted open-shell Hartree-Fock (ROHF). These advancements address the convergence issues of traditional △SCF methods and eliminate spin contamination present in unrestricted open-shell △SCF (U△SCF). Through a series of benchmarks, it has been found that for primarily single excitations of orbitals: for singlet excitations in the valence shell, these restricted open-shell methods achieve accuracy comparable to TDDFT; for triplet states, Rydberg states, singlet−triplet gaps, charge transfer states, core excited states and double excited states, these restricted open-shell methods are significantly more accurate than TDDFT.

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Electronic structure of periodic systems containing strongly correlated transition metals

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We present the Effective Hamiltonian of Crystal Field (EHCF) method, a hybrid embedding quantum chemical method developed for an accurate treatment of strongly correlated *d*-shells of transition metal (TM) atoms embedded into periodic systems [1]. EHCF is based on dividing a space of one-electronic states in two subspaces separately spanned by *d*- and *s, p*- atomic orbitals. The many-electron wave-function of the correlated *d*-system is expressed in the configuration interaction form, while the *s, p*- subsystem is described by the Hartree-Fock single-reference wave-function. Resonance interactions between subsystems are considered by the Löwdin partitioning technique combined with the Green's function formalism [1].

Our results for a series of TM oxides and TM dopants in oxide materials demonstrate the ability of the EHCF method to accurately reproduce the spin multiplicity and spatial symmetry of the ground state as well as energies and multiplicities of the excited *d*-states. For the studied materials, the calculated *d-d* transitions agree with the lines observed in optical spectra [1]. For iron-containing compounds our calculations allow to reproduce values and temperature dependence of ^{57}Fe Mössbauer quadrupole splitting observed in experiment.

We apply EHCF to investigate carbodiimides and hydrocyanamides of transition metals [2], spin-crossover in metal organic frameworks, transition metal dopants suitable for quantum computing applications. We also discuss future perspectives of the EHCF method and its place in the context of modern solid state quantum chemistry and physics.

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Density-Based Many-Body Expansion as a Case Study on Interoperability

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Quantum-chemical subsystem and embedding methods depend heavily on interoperable software and standards [1]. They are at the focal point of our scripting framework PyADF. To ensure efficiency and therefore sustainability in the development of subsystem methods, one must avoid implementing the employed methods from scratch, especially when combining different levels of theory. This and other general best practices in software development need to be kept in mind, which illustrates a challenge that is faced throughout the field.

The density-based many-body expansion is a subsystem and embedding method designed to describe large and complex molecular clusters accurately and efficiently [2]. Its basic idea is highly adaptable and was abstractly implemented in PyADF. Here, we present its further development based on well-established, interoperable, and actively supported standards and tools, like pyscf, libxc, and the molden format. With its recent application to CCSD(T) calculations [3], we have demonstrated the method's adaptability and potential. The modular approach curbs the cost of development for upcoming features, such as gradients and structural optimization.

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Developments of approaches for structural relaxation of excited states of materials based on embedded cluster model

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Broadband photo-luminescence phenomena of metal halides is usually related to the forming of self-trapped excitons (STE). In order to understand the STE emission mechanism, relaxation of excited states geometry of materials becomes important. Widely used method nowadays for this topic is occupancy-constrained-DFT (OC-DFT) which has shortcomings such as lack of rigorous theoretical foundation, convergence issues and disability to obtain the complete potential surfaces for excited states. On the other hand, usage of rigorous theoretical methods with higher accuracy are limited due to their high computational cost in solids. Embedded cluster methods separate the total system into active cluster as well as environments and include the effects on cluster from environments in specific ways. These methods make it possible to apply accurate methods with highly demanding computational cost to structural relaxation of localized excited states of materials.

In this work, an embedded cluster model (ECM) based on ab initio model potential (AIMP) and a grid of point charges is built. The validity of this approach is tested using NaF:Cu$^+$ as an example. In this model, $[CuF_6]^{5-}$, which determines the spectral properties of NaF:Cu$^+$, is set to be cluster. Ions around this cluster within 10 Å are represented as environments to generate AIMPs, which take into consideration the Coulomb and exchange effects on cluster from environments as well as the repulsion from Pauli principle. Farther ions are treated as point charges and a layer of ions as surface charges are generated through fitting the electrostatic potential to make the system neutral and eliminate dipole moment of the whole model. Combined with time-dependent density-functional theory (TDDFT), equilibrium geometry of ^3E_g state of $[CuF_6]^{5-}$ cluster is obtained. Absorption and emission energies of NaF:Cu^+ are calculated as well. We also calculate the excitation energies considering spin-orbit coupling effect by using noncollinear TDDFT.

Nonadiabatic Field on Quantum Phase Space

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Nonadiabatic dynamics plays a crucial role in the investigation of various significant photochemical processes in chemistry, biology and material science. We present two recent advances in the development of trajectory-based nonadiabatic dynamics methods. One significant development is the establishment of the generalized coordinate-momentum phase space representation for molecular systems [1-7]. This formalism describes both nuclear and electronic degrees of freedom (DOFs) using continuous coordinates and momenta. The normalization of electronic phase space results in a smooth manifold, which is diffeomorphic to a submanifold of the U(F) group. The other advancement is the development of nonadiabatic field (NaF) [8,9]. This approach decomposes the force acting on nuclei into two components: the adiabatic force originating from a single electronic state, and the nonadiabatic force arising from the nonadiabatic coupling field. NaF integrates the benefits of both Born-Oppenheimer dynamics and mean-field dynamics. By implementing NaF in the generalized coordinate-momentum phase space representation, the resulting novel method demonstrates superior performance compared to conventional methods in numerical simulations of various model systems, including condensed phase dissipative systems, cavity quantum electrodynamics models, gas-phase scattering models, and molecular conical intersection models.

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Mechanistic Insights into Twisted Intramolecular Charge Transfer in CBP and its derivatives

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Organic light-emitting diodes (OLEDs) are crucial components in modern electronic displays, where effective charge transfer plays a pivotal role in their performance. Carbazole-based host materials, such as 4,4′-bis(N-carbazolyl)-2,2′-biphenyl (CBP), are commonly used for their strong charge transfer capabilities, though their lower triplet energy levels can limit their effectiveness [1]. To address this, higher triplet energy materials like 4,4′-bis(9-carbazolyl)-2,2′-dimethyl-biphenyl (CDBP) and 3,3′-bis(9H-carbazol-9-yl)biphenyl (mCBP) have been developed [2]. However, the detailed mechanisms underlying charge transfer and structural changes in these materials remain insufficiently explored, emphasizing the need for fundamental studies. Using time-dependent density functional theory (TD-DFT) and nonadiabatic molecular dynamics (NAMD) simulations, our research reveals that in CBP, charge transfer occurs in the S_1 state following a rapid internal conversion from the S_n state, leading to the planarization of the biphenyl group on a picosecond timescale. Additionally, we observed that the emission spectra of CBP broaden and red-shifted with increasing solvent polarity, indicating that charge transfer and structural changes are more pronounced in polar solvents. In contrast, in CDBP and mCBP, where π-conjugation is disrupted, charge transfer is significantly limited. Consequently, the absorption and emission spectra of these materials retain their vibronic structure, regardless of solvent polarity, suggesting structural distortion is minimal. This study provides deeper insights into the ultrafast charge transfer processes and associated structural changes in CBP, advancing our understanding of the photophysical properties of these critical OLED host materials.

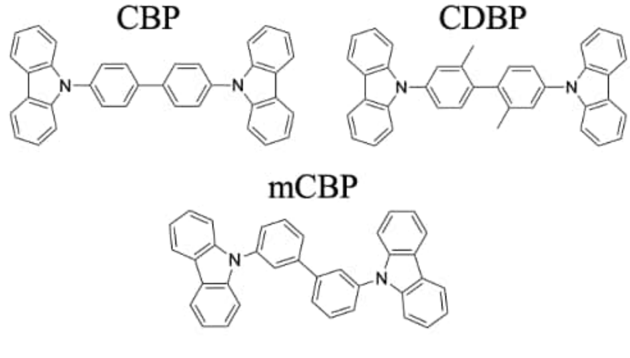

Figure 1, molecular structure of CBP, CDBP and mCBP.

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Building Accurate Molecular Simulation Models for Studying Warm Cloud Seeding

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Climate change has intensified extreme weather events including both droughts and floods, prompting efforts to develop effective mitigation strategies. Recently, different parts of the world including China have been experimenting with cloud seeding to induce precipitation. While cold cloud seeding with agents like silver iodide (AgI)[1] has been extensively studied, the molecular mechanisms underlying warm cloud seeding, which involves the coalescence of water droplets without ice formation, remain poorly understood.

This project seeks to bridge this knowledge gap by developing simulation models to study warm cloud seeding. Our methodology integrates expensive quantum mechanical (QM) calculations to generate reference data on small scales and use the data for parametrizing classical force fields that will be used for larger length and time scales. By investigating the effects of inorganic salts and charged organic matter on water droplet behavior, including water uptake and coalescence dynamics, we aim to enhance our understanding of droplet interactions in the atmosphere and the properties at the air-water interface, thereby providing deeper insights into warm cloud seeding and its potential applications.

This research was supported by a General Research Fund from The Research Grants Council of Hong Kong (14300823).

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Correlation Functions From Tensor Network Influence Functionals: The Case of the Spin-Boson Model

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We present an investigation into the use of matrix product state (MPS) representations of influence functionals (IF) for calculating real-time equilibrium correlation functions in open quantum systems. Our study centers on the unbiased spin-boson model and explores the application of IF-MPS for complex time propagation and the construction of correlation functions in the steady state. We analyze three distinct IF approaches: the process tensor method, which uses the Kadanoff-Baym contour to target correlation functions at all times; a method utilizing a complex contour for evaluating the correlation function at a specific time; and a steady-state formulation that bypasses imaginary or complex times while enabling access to correlation functions at all times. Our results demonstrate that within the IF framework, the steady-state formulation offers a robust technique for evaluating equilibrium correlation functions. This presentation is based on a paper available on arXiv. [1]

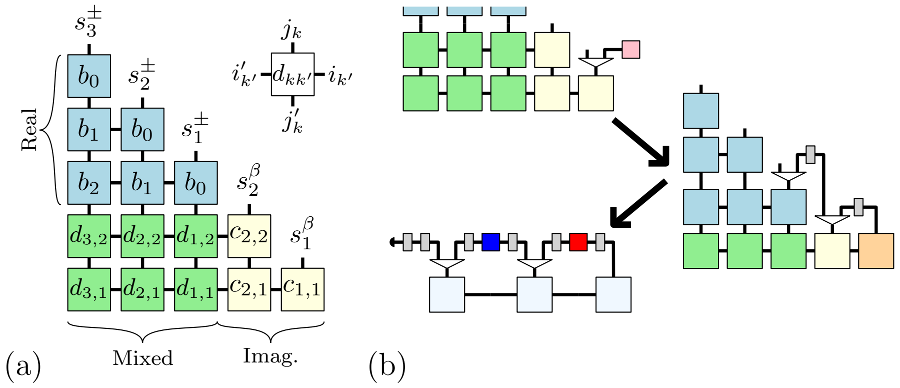

Figure 1. A schematic diagram of the process tensor method.

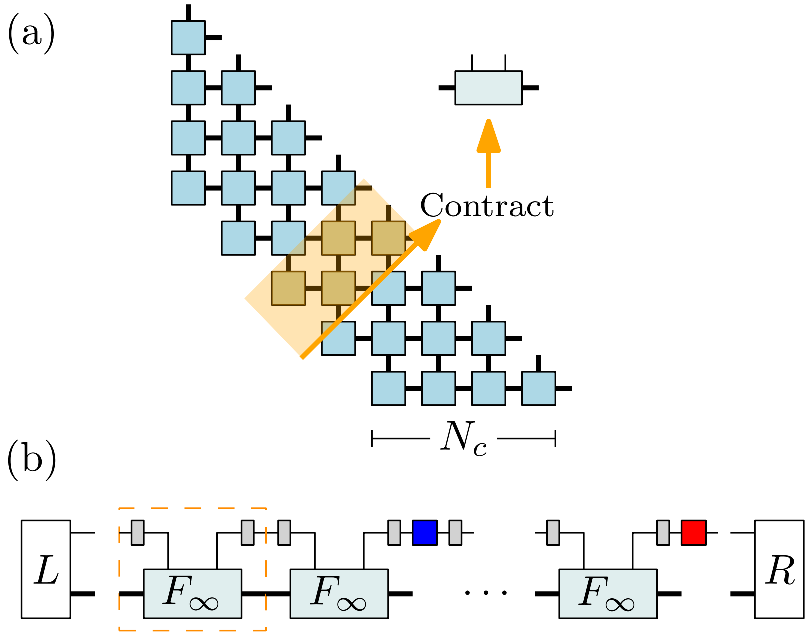

Figure 2. A schematic diagram of the steady state method.

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Time-Dependent Density Matrix Renormalization Group Method for Quantum Transport with Phonon Coupling in Molecular Junction

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Quantum transport in molecular junctions has attracted great attention. The charge motion in molecular junction can cause geometric deformation, leading to strong electron phonon coupling, which was often overlooked. We developed a nearly exact method to calculate the time-dependent current and occupation number for molecular junction modeled by electron-phonon coupled bridge state using time-dependent density matrix renormalization group (TD-DMRG) method within grand canonical ensemble. The oscillation period and amplitude of the current are found to be dependent on the electron phonon coupling strength and the energy level alignment with the electrodes.

We came up with a new approximation to give a thorough explanation of all these phenomena and use it to predict the bistability phenomenon and the behavior of steady currents in the strong electron phonon coupling regime. The results, compared with results from non-equilibrium Green's Function (NEGF) and polaron transformation, proved its superiority.

At finite temperature, we utilized the special model of molecular junction systems and thermal field dynamics, as well as the thermal Bogoliubov transformation of Fermi and bosons at the same time, to improve computational efficiency at finite temperatures.

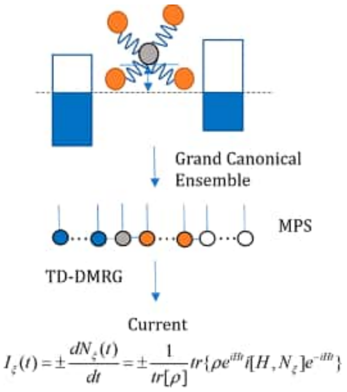

Figure 1. Quantum Transport with Phonon Coupling in Molecular Junction and its mapping into MPS.

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Solvated Electron from First Principles and Machine Learning

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The nature of the hydrated electron has been a challenge for both experiment and theory due to its short lifetime, high reactivity, and the need for a high level of electronic structure theory to achieve predictive accuracy. The lack of a classical atomistic structural formula makes it exceedingly difficult to model the solvated electron using conventional empirical force fields, which describe the system in terms of interactions between point particles associated with atomic nuclei. Here, we overcome this problem using a machine-learning model that is sufficiently flexible to describe the effect of the excess electron on the structure of the surrounding water, without including the electron explicitly in the model. The model is not only able to reproduce the stable cavity structure but also recovers the correct localization, vibrational, and charge-transfer-to-solvent dynamics at the accuracy of the correlated wave function or hybrid functional method. It is sufficiently inexpensive to afford a full quantum statistical and dynamical description and allows us to achieve accurate determination of the structure, dynamics, and temperature-dependent properties of the solvated electron.

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Real-time time-dependent density functional theory for x-ray absorptions

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Real-time time-dependent density functional theory (RT-TDDFT) can, in principle, access the whole absorption spectrum of a many-electron system exposed to a narrow pulse. However, this requires an accurate and efficient propagator for the numerical integration of the time-dependent Kohn–Sham equation. While a low-order time propagator is already sufficient for the low-lying valence absorption spectra, it is no longer the case for the x-ray absorption spectroscopy (XAS) of systems composed even only of light elements, for which the use of a high-order propagator is indispensable. It is then crucial to choose a largest possible time step and a shortest possible simulation time so as to minimize the computational cost. To this end, we propose here a robust AutoPST approach to determine automatically (Auto) the propagator (P), step (S), and time (T) for relativistic RT-TDDFT simulations of XAS.

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A stochastic Schrödinger equation and matrix product state approach to carrier transport in organic semiconductors with nonlocal electron-phonon interaction

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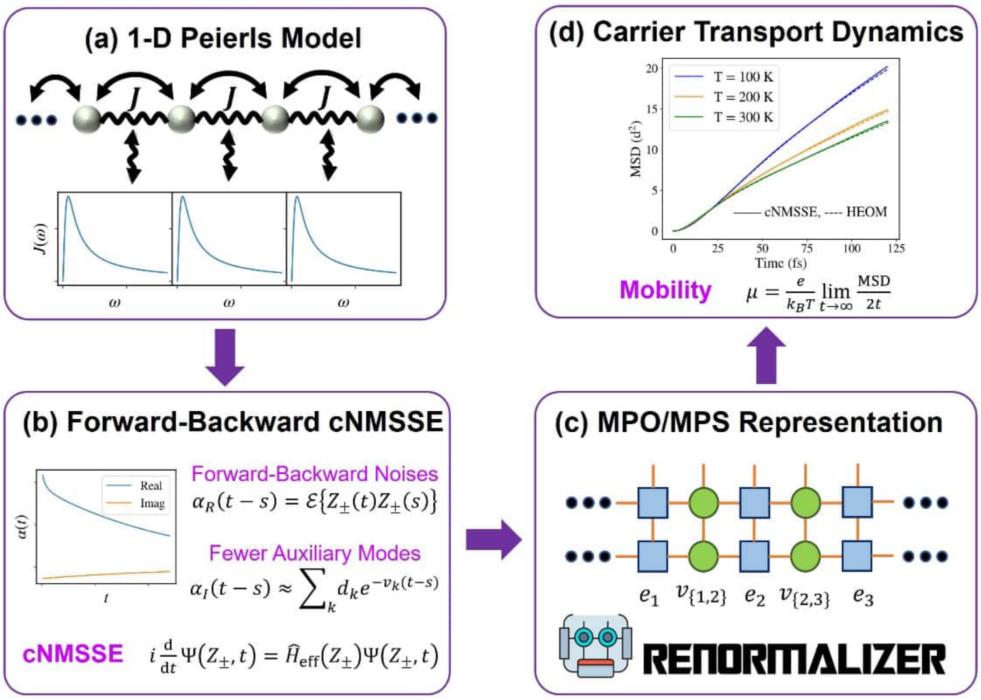
We present a numerically nearly exact approach to investigate carrier transport dynamics in organic semiconductors by extending the non-Markovian stochastic Schrödinger equation with complex frequency modes (cNMSSE) to a forward-backward scheme, and solving it using the matrix product state (MPS) approach. By utilizing the forward-backward formalism for noise generation, the bath correlation function can be effectively treated as a temperature-independent imaginary part, enabling a more accurate decomposition with fewer complex frequency modes. Using this approach, we study the carrier transport and mobility in the one-dimensional Peierls model, where the nonlocal electron-phonon interaction is taken into account.



Non-unique Hamiltonians for discrete symplectic dynamics

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An outstanding property of any Hamiltonian system is the symplecticity of its flow, namely, the continuous trajectory preserves volume in phase space. Given a symplectic but discrete trajectory generated by a transition matrix applied at a fixed time-increment ($\tau > 0$), it was generally believed that there exists a unique Hamiltonian producing a continuous trajectory that coincides at all discrete times ($t = n\tau$ with n integers) as long as τ is small enough. However, it is now exactly demonstrated that, for any given discrete symplectic dynamics of a harmonic oscillator, there exist an infinite number of real-valued Hamiltonians for any small value of τ and an infinite number of complex-valued Hamiltonians for any large value of τ. In addition, when the transition matrix is similar to a Jordan normal form with the supradiagonal element of 1 and the two identical diagonal elements of either 1 or −1, only one solution to the Hamiltonian is found for the case with the diagonal elements of 1, but no solution can be found for the other case. [1].

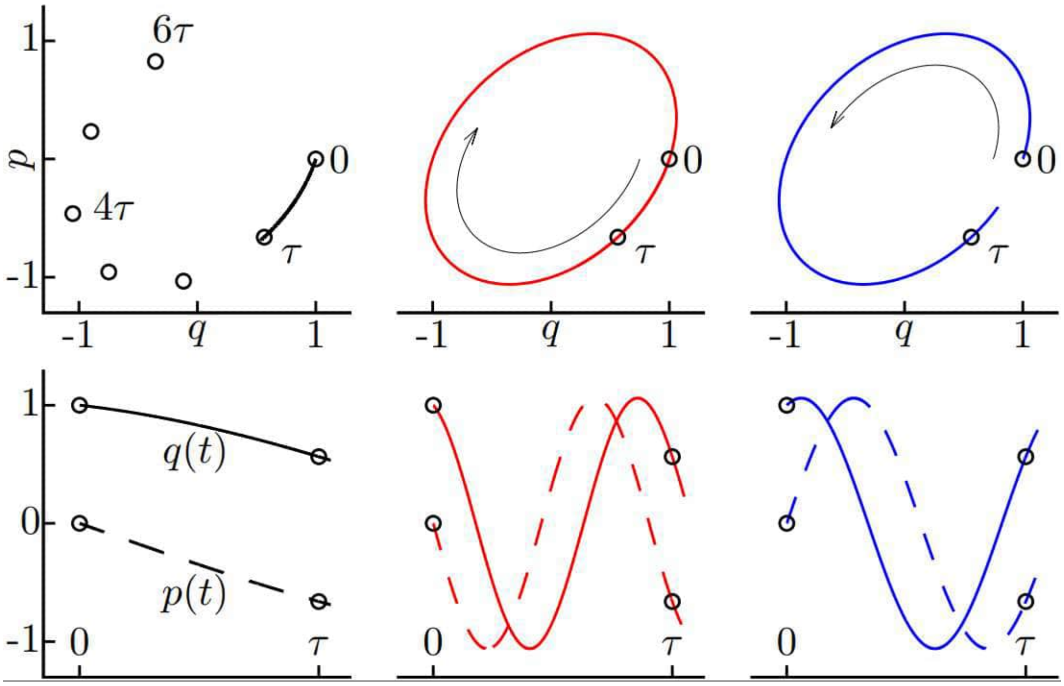

Figure 1. Typical continuous trajectories from $[q(0) = 1, p(0) = 0]$ to $[q(1.05\tau), p(1.05\tau)]$ in the qp phase space (top) and as functions of time [bottom, solid lines for $q(t)$ and dashed $p(t)$] generated by the Hamiltonians of Eq. (5) at $m = 0$ (left), 1 (middle, red), and -1 (right, blue). In the phase space, the trajectory of the phase points rotates clockwise ($m \geqslant 0$) and counterclockwise ($m<0$).

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An Electronic Spin on Geometric Phase Effects in Molecular Systems

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Molecules are inherently geometric in nature, as their properties are not only determined by their atomic composition but also their three-dimensional arrangement in space. However, the geometry arising from the atomic configuration alone is rather mundane, essentially being given by a tuple of Cartesian coordinates. A more exotic type of geometry emerges from the interplay between the nuclear coordinates and the electronic wave function. It is known, for instance, that the electronic wave function may not return to its initial state when transported around a closed contour in nuclear coordinate space, with the difference given by a phase factor.[1] This phase factor is geometric in nature only depending on the path taken in nuclear coordinate space and bearing some resemblances to the notion of curvature in Riemannian manifolds. When the nuclear motion is treated quantum mechanically according to the Born–Oppenheimer approximation, the geometric phase translates to an effective vector potential describing a pseudo-magnetic interaction with the nuclei. It can be argued that interactions of this type are most relevant if the electronic wave function is complex-valued, which, for instance, occurs if there is a conical intersection or if spin-orbit coupling is included.[2] Using a simple triatomic toy-model that exhibits a conical intersection at equilateral configuration, I will illustrate why geometric phase effects necessarily occur under these conditions. In addition, the results presented in this poster will be formulated using fibre bundles, providing a mathematical yet approachable perspective to the geometric phase effect.

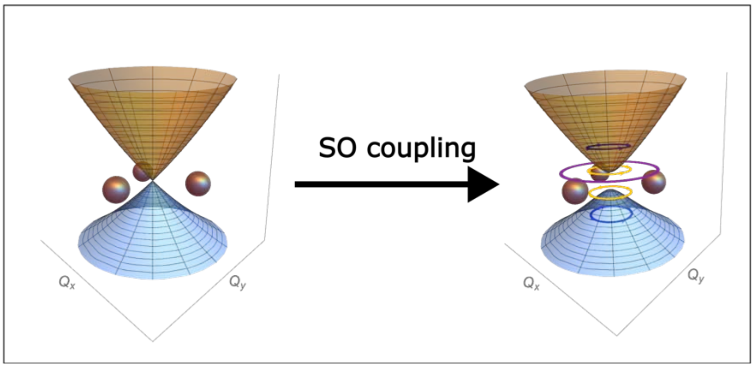

Figure 1. The effect of spin-orbit coupling on the triatomic model system

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Excursions in Polaritonic Chemistry: From Relaxation in Liquids to Chemical Kinetics

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Recent years have shown how chemical kinetics can be modified using optical microcavities— devices capable of confining light at different resonant frequencies. By matching the frequency of light to a molecular vibration, strong coupling at resonance leads to the formation of hybrid light-matter states known as polaritons, often coinciding with either the suppression or enhancement of reaction rates. This presentation presents two works [1,2] that examine this emerging phenomenon of "polaritonic chemistry." In the first work, we examine how the properties of supercooled liquids—the state of a liquid when cooled below freezing—can be modified in such cavities [1]. Here, we use cavity molecular dynamics (CavMD) [3], which provides a classical treatment of the light-matter system. Our findings suggest a critical coupling strength in which liquids can relax faster at equilibrium. The second work explores further the quantum nature of the light-matter interactions, applying mixed quantum-classical (MQC) methods to study a toy model for chemical reactions in microcavities [2]. Our findings suggest that treating the photon quantum mechanically as well as employing a multi-state version of the mapping approach to surface hopping (MASH) [4] are vital to obtaining rates much closer to the full quantum mechanical treatment of the problem.

[1] In collaboration with Prof. Norah Hoffmann at NYU

[2] In collaboration with Profs. Arkajit Mandal and David Reichman, at Texas A&M and Columbia University, respectively.

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Early Stages of Battery Electrolytes Degradation: Theory and Experiment

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The electrochemical stability window (ESW) is an important characteristic of electrolytes in general and particularly of battery electrolytes. It is believed that within this voltage window no redox processes involving the electrolyte components occur. However, the literature data available for the ESWs of standard electrolytes are very ambiguous as the measurements depend on a number of factors and there is no established protocol for the experimental assessment of this property.

Recently, tailored EPR experiments registered the presence of radicals in lithium- and sodium-ion batteries electrolytes even in the voltage ranges considered to be their respective ESWs [1]. Apparently, these radicals are products of the partial degradation of the solvents but the salts employed also play a role, because dissimilar radicals were identified upon the utilization of different salts. Knowledge about these redox reactions is very important for the battery safety and durability. Combining experimental techniques (EPR, LSV, CV) and molecular modelling (DFT), this study aims at clarifying the type and mechanism of the redox processes taking place within the ESWs of the most typical electrolytes used in lithium- and sodium-ion batteries.

The study is carried out with the financial support of the Bulgarian National Science Fund, contract CARiM (NSP VIHREN, КП-06-DB-6).

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Stability and ion conductivity of novel Li_6PIO_5: A DFT study

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In this study, we employ a computational search utilizing Density Functional Theory (DFT) to uncover promising solid-state electrolytes for advanced energy storage devices. Focusing on oxide materials, we investigate the potential of Li_6PIO_5 as a stable and high-conductivity electrolyte. Motivated by recent findings highlighting the superior ion conductivity of Li_6PbrO_5 [1], we propose the substitution of bromine with iodine in Li_6PIO_5, anticipating similar favorable properties. Through thorough computational simulations, including substitution and structural relaxation within the framework of density functional theory, we demonstrate the stability of Li_6PIO_5 by placing it on the stability convex hull diagram. Furthermore, phonon dispersion calculations validate the stability of the material by confirming all positive frequencies. Expanding our exploration, we explore other compositions within the Li-P-I-O system, unveiling novel metastable structures such as Li_7PO_6. To further investigate the ion conductivity, we introduced lithium vacancies into each structure, which reveals that these vacancies slightly increase the conductivities. Additionally, the conductivity was found to be temperature-dependent, increasing proportionally with temperature. Distortion studies were achieved through controlled alteration of one iodine atom position, from 4a to 4c Wyckoff position [2]. An assessment of the electrochemical stability window reveals a high value of approximately 4 eV, further establishing the viability of Li_6PIO_5 as a prospective solid-state electrolyte. In summary, our findings substantiate the candidacy of Li_6PIO_5 as a promising electrolyte material, offering potential advancements in energy storage technology.

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Disordered structure reduces the bandgap of double perovskite $Cs_2AgBiBr_6$ through wavefunction localization

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$Cs_2AgBiBr_6$ is the most extensively studied halide double perovskite, notable for its microsecond carrier lifetime and excellent environmental stability. Nevertheless, $Cs_2AgBiBr_6$ suffers from a relatively large bandgap (about 2.0 eV), resulting in low light absorption and limiting its photovoltaic and optoelectronic performance. It has been reported that the bandgap of $Cs_2AgBiBr_6$ can be dramatically reduced through lattice reconfiguration under pressure or thermal treatment. These observations are attributed to the creation of disordered structure by randomly switching the Ag and Bi atoms in the lattice, while experimental characterizations can hardly identify such sophisticated changes. We employ density functional theory (DFT) calculations to theoretically investigate the impacts of disordered structure on $Cs_2AgBiBr_6$. We demonstrate the Ag and Bi atoms exhibit quite different interactions with the adjacent Br atoms, and the random structure leads to significant lattice distortion. Such structural changes break the lattice symmetry and split the degenerate energy levels. Moreover, the segregated Ag and Bi atoms form some cluster configurations and produce localized electronic states. These states serve as new band edges and reduce the bandgap, rationalizing the experimental observations. Our results shed light on understanding and manipulating the electronic properties of disordered materials.

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A Theoretical Study on Proton Transfer Reactions in Anthracene-Urea Derivatives

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An excited-state proton transfer (ESPT) reaction, which occurs in the excited states of molecules, is of significant interest in both chemistry and biology, particularly in the context of light-driven reaction control. An intermolecular ESPT reaction has been identified from the dual fluorescence peaks observed using fluorescence lifetime measurement. In our previous studies, we simulated the ESPT reaction of 1-anthracen-n-yl-3-phenylurea (*n*PUA; n = 1, 2, 9) [1, 2] and an acetate ion by calculating the acid dissociation constant in the lowest excited state (pK_a*) [3]. The proton-transferred structure was found to be less stable than the initial structure, which did not agree with the experimental data. We attributed this discrepancy to the lack of solvent effects in our model. To investigate this hypothesis, we carried out molecular dynamics (MD) simulations to obtain a better understanding of the solvation structure of the nPUA-acetate ion complex. We performed MD simulations on nPUA and an acetate ion to obtain intermolecular distances and determine whether the intermolecular hydrogen bond is influenced by the solvent molecules. Detailed results from these simulations will be presented in the poster session.

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Theoretical study on the effect of ring modification in cuprous halide complexes on the TADF mechanism

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In recent years, researchers have paid much attention on obtaining highly efficient OLEDs fabricated with TADF Cu(I) halide complexes. Although the TADF properties of Cu(I) halide complexes can be enhanced by changing substituents on the ligands, how to achieve high quantum efficiency and short decay lifetime remains a challenge. Here, we focused on investigating the influence of ring modifications in Cu(I) chloride complexes containing bidentate phosphorus (P^P) ligands on the TADF mechanism with the use of electronic structure calculations. The results indicate that enhancing the electron-withdrawing effect of ring in the complexes can effectively suppress structural deformation between the S_1 and T_1 states and strengthen the charge-transfer characteristics of the complexes, leading to a reduction in ΔE_{ST}. Additionally, the electron-withdrawing effect effectively suppress the in-plane bending vibrations of the P_3(PH)3 ligand, leading to a gradual decrease in structural deformation and reorganization energy as the electron-withdrawing effects increase. Ultimately, the complexes achieve faster intersystem crossing and reverse intersystem crossing rates. Our study reveals that enhancing electron-withdrawing effects of ring in the complex can effectively improve the TADF properties of Cu(I) chloride complexes, which provides valuable theoretical guidance for the design and synthesis of Cu(I) halide complexes with efficient TADF properties.

Review on Improving the Performance of SiOx Anodes for a Lithium-Ion Battery through Insertion of Heteroatoms: State of the Art and Outlook

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Lithium-ion batteries (LIBs) are essential for devices ranging from mobiles to electric vehicles. However, traditional graphite anodes, capped at 372 mAh/g, are inadequate for higher capacity demands. Silicon-based anodes could theoretically provide over 4200 mAh/g but suffer from 400% volume expansion and mechanical stress and unstable SEI layer formation. Silicon-oxide (SiO_x) anodes, featuring a multiphase structure of amorphous Si and SiO_2, help curb volume expansion and boost cyclability via lithium silicates formation. Despite benefits, challenges like low initial coulombic efficiency and the need for pre-lithiation call for advanced solutions. Recent advances in both experimental and theoretical research have significantly enhanced the microstructure and chemical properties of SiO_x anodes, leading to improved electrochemical performance and durability. This review highlights these advancements, focusing on their potential to revolutionize LIBs technology by enhancing understanding of lithiation/delithiation processes and SiOx structure behavior. [1].

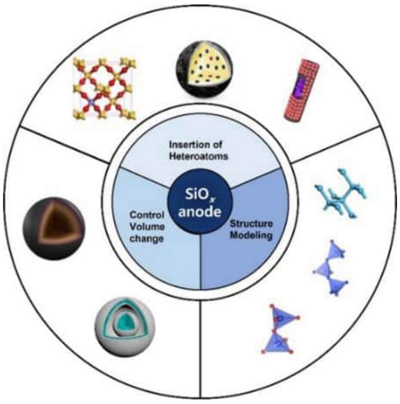

Figure 1. Overview of SiO_x anode heteroatom doping strateges.

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Theoretical study on singlet fission dynamics in finite-size molecular aggregates with various intermolecular interaction strengths and structures

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Singlet fission (SF) is a photophysical process where one singlet exciton (S_1) splits into two triplet excitons ($2T_1$) via correlated triplet pair (TT) states. Numerous studies have focused on the mechanism of SF dynamics [1]. In this study, we theoretically investigated SF dynamics in finite-size molecular aggregates. Based on the quantum master equation (QME) simulation, we examined how the intermolecular interaction strengths and structures affect the energies and wavefunctions of exciton states and the time evolution of the TT population. We considered linear and circular molecular aggregates [2,3] where symmetry reduction or site-dependent electronic coupling was introduced. We also discussed the spatial distributions of TT states for these aggregates.

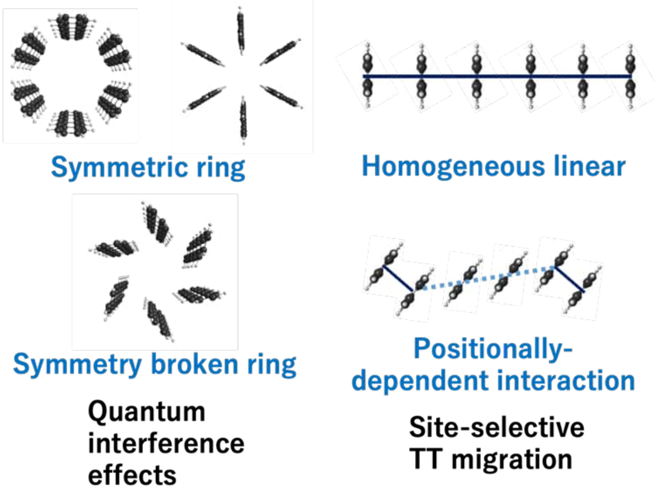

Fig. 1 Molecular aggregate models examined in this study.

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A Molecular Dynamics Simulation on the Stress Corrosion Cracking Mechanism of BCC-FCC type Dual-phase High-Entropy Alloys

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BCC-FCC type dual-phase high entropy alloys, such as AlCrFeNi, exhibit excellent high-temperature strength, making them potential for structural materials under extreme conditions. However, under combined stress and corrosive environments, the damage of structural materials which is called stress corrosion cracking (SCC) may lead to catastrophic failure. Understanding SCC mechanisms is vital to prevent failure, yet is challenging to achieve the atomic scale by experiments. Therefore, this study employs molecular dynamics to investigate the SCC mechanism of BCC-FCC type dual-phase high entropy alloys under high-temperature and high-pressure water environment.

A dual-phase model combined with $Al_2CrFeNi_2$ BCC crystal and $AlCr_2Fe_2Ni$ FCC crystal was built (Fig. 1) imitating the structure observed in experimental study [1]. Here the BCC crystals majorly comprise Al and Ni, and the FCC crystals are predominantly composed of the Fe and Cr. Pre-crack was introduced along the grain boundary. The alloy models are placed in both vacuum and water environments, where the density of water is $0.334 g/cm^3$. Tensile simulations were then conducted on both models at 650 K, 25 MPa along y direction.

Fig. 2 shows the crystal structures at 7.0% strain. Both models exhibit a phase transition from BCC to FCC and HCP (left parts of Fig. 2(a) and (b)). However, the FCC crystal on the right behaves differently in vacuum and water. In vacuum (Fig. 2(a)), HCP stacking faults are generated along $(111)^{FCC}$; in contrast, in water (Fig. 2(b)), HCP stacking faults only appear internally, and a phase transition to BCC occurs near the surface. This is because the oxidized layer inhibits Schottky dislocation formation, making it difficult to generate stacking faults so that another way has to be found to relax the tensile stress [2]. A comparison between the SCC mechanism of dual-phase and single-phase alloys will be reported at the meeting.

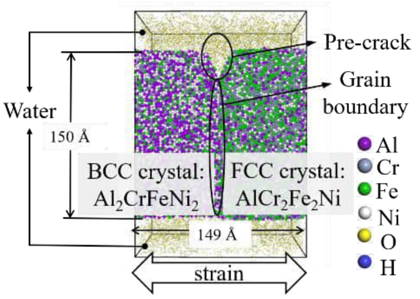

Fig. 1 AlCrFeNi dual-phase alloy in water

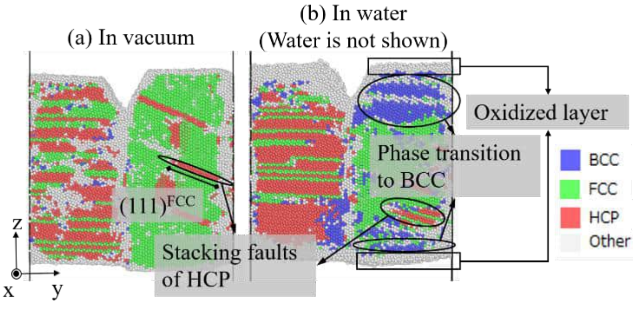

Fig. 2 Crystal structures at 7.0% strain AlCrFeNi high-entropy

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Modelling of sodium clusters in various conjugated carbonaceous structures

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Sodium-ion batteries (SIBs) are emerging as a prospective alternative to lithium-ion batteries for many applications, including electric cars and stationary energy storage. Improving all components of SIBs is crucial for their future. Anode materials deserve special attention. A very promising candidate is the nongraphitizable carbon, also called hard carbon – a disordered form of carbon which does not turn into graphite even at very high temperatures. Important structural features of hard carbon are the presence of nano-sized graphitic domains, various defects, and multiple pores allowing the migration of ions larger than lithium. An important advantage of hard carbon, regarding its price and availability, is that it can be obtained by pyrolysis of organic wastes such as wood pulp, coffee grounds, walnut shells and others.

A peculiar feature of the insertion of Na in hard carbon is the substantial plateau capacity below 0.1 V (vs Na^+/Na) observed in the charge-discharge curves. Some authors suggest that it is due to Na-intercalation into the graphitic domains; others ascribe it to Na-clusters formation in the micro-pores which we consider a more likely explanation and attempted to model and analyze. Fullerene fragments, nano-cones, and nanotubes were used as pore models. By means of DFT, the size-dependent stability of carbon-caged Na-clusters and the energetics of cluster growth in different carbonaceous fragments is discussed.

Acknowledgements: The study is supported by the Bulgarian Science Fund, project CARiM/VIHREN, КП-06-ДВ-6/2019 and project КП-06-ПН-69/9, and by the Science fund of University of Sofia project 80-10-2/29.03.2024.

Assessing short-range charge transfer character of potential MR-TADF emitters with wavefunction descriptors

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Multiresonance thermally-activated delayed fluorescence (MR-TADF) emitters have gained popularity given their potential of attaining negligible adiabatic singlet-triplet energy gaps, i.e., ΔE_{ST} – thus, increasing the reverse and direct intersystem crossing rates – without affecting fluorescence [1]. This is achieved due to the singlet and triplet states' short-range charge transfer character (SRCT). Thus, obtaining quantitative information about SRCT would help develop new MR-TADF emitters. This work studies three different MR-TADF emitters: DOBOA, DiKTa and OQAO.

In this work, we compute their adiabatic ΔE_{ST} with four different methods (TDA-CAM-B3LYP, STEOM-DLPNO-CCSD, ADC(2) and SCS-CC2) and we propose the use of two wavefunction descriptors – Q_a^t and LOC$_a$ – based on the 1-particle transition density matrix [3], which assigns the amount of charge centered on the atoms. We compute these descriptors for three transitions: $S_0 \rightarrow S_1$, $S_0 \rightarrow T_1$, and $S_1 \rightarrow T_1$. For the studied cases, these descriptors are independent of the choice of electronic structure method and optimal geometry. We show that the adiabatic ΔE_{ST} decreases with the increase of $S_1 \rightarrow T_1$ Q_a^t, while ΔE_{ST} increases with an increase of the $S_0 \rightarrow T_1$ Q_a^t. These trends showcase how the Q_a^t values can act as guiding descriptors to design new MR-TADF emitters with small ΔE_{ST} values.

Moreover, we compute fluorescence, direct, and reverse intersystem crossing rate constants assessing the effect of different approximations [2].

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XEDA: an efficient and flexible energy decomposition analysis (EDA) toolkit

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In recent years, our research group has developed a series of energy decomposition analysis methods for the study of the nature of various complex environmental molecular interactions [1-3]. In our methods, only requires the energy and density matrices of monomers and supramolecule, and then can efficiently compute electrostatic, exchange, repulsion, polarization, and correlation terms. These methods are included in our program XEDA. This program can used for doing DM-EDA, BLW-ED and their extensions. XEDA can be used for bio-chemistry systems by using QM/MM and can do real-space analysis to get qualitative pictures. This program is written with C language and python API is given for more flexible use.

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Sub- and Supercritical Water Structure Calculated using the Self-Learning Path Integral Hybrid Monte Carlo Method

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The inclusion of nuclear quantum effects (NQEs) is necessary in modelling water and its isotopologues, due to the low mass of hydrogen and the significant mass difference with its isotopes, deuterium (D) and tritium (T). Previously, we demonstrated that the auto-ionization constant (pK_w) for water changes several orders of magnitude with the inclusion of NQEs [1]. The equilibrium structure of water, and especially its hydrogens, have also been found to be influenced by NQEs [2] even under sub- and supercritical conditions [3]. However, performing the ab initio path integral molecular dynamics (AI-PIMD) simulations needed to model NQEs is computationally intensive. To address this the self-learning hybrid Monte Carlo using a mixed ab initio and machine learned potentials (SL-PIHMC-MIX) method has been proposed. Here, we apply it to the simulation of sub- and supercritical water, where we are able to probe the accuracy of several DFT functionals in describing the structure of high temperature water, including NQEs. The SL-PIHMC-MIX method extends our previous self-learning hybrid Monte Carlo SL-HMC [4] to the path integral regime, and enables the study of larger systems through the potential mixing. Both methods converge the structure of water with (SL-PIHMC-MIX) and without (SL-HMC) NQEs using only a tenth of the ab initio calculations needed to converge from AI-PIMD or AI-MD studies, while exactly reproducing the results from AI-PIMD and AI-MD.

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Towards ML- and QML-accelerated discovery of catalytic materials and mechanisms

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Our attempts to build somewhat realistic models of surface- and nano-catalysis at finite temperature will be reviewed. We are bringing in machine learning (ML), most notably active learning (AL) to, ultimately, define the relevant reaction coordinates. We report progress made on a longer journey towards this goal, by using AL for the global optimization of nanocatalysts such as Ni-CeO_2, including vacancies and interactions with water, on the one hand, and data-base searches for better materials for thermo-, electro-, photo-activated catalysis, on the other. Developed protocols and software, QMLMaterial, GAMaterial, MLChem4D and RLMaterial will be highlighted. Initial forays into ML on quantum computers (QAL) will be highlighted. Our efforts to date are reported in fifteen papers, among which: [1-4].

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Breaking the Size Limitation of Non-Adiabatic Molecular Dynamics in Condensed Matter Systems with Local Descriptor Machine Learning

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Non-adiabatic molecular dynamics (MD-NA) application to condensed phase has drawn tremendous attention recently. Studies of condensed matter allow one to employ efficient computational tools, such as density functional theory (DFT) and classical path approximation (CPA). Still, system size and simulation timescale are strongly limited by costly ab initio calculations of electronic energies, forces, and NA couplings. We resolve the limitations by developing a fully machine learning (ML) approach in which all the above properties are obtained using neural networks based on local descriptors. Trained on small systems, the neural networks are applied to large systems and long timescales, extending NA-MD capabilities by orders of magnitude. We demonstrate the approach with dependence of charge trapping and recombination on defect concentration in MoS_2. Charge trapping slows with decreasing defect concentration; however, recombination exhibits complex dependence, conditional on whether it occurs between free or trapped charges, and relative concentrations of carriers and defects. Completely ML based, the approach bridges the gap between theoretical models and realistic experimental conditions, and enables NA-MD on thousand atom systems and many nanoseconds.

[1] Dongyu Liu, Bipeng Wang, Yifan Wu, Andrey S. Vasenko, Oleg V. Prezhdo. "Breaking the Size Limitation of Non-Adiabatic Molecular Dynamics in Condensed Matter Systems with Local Descriptor Machine Learning". *Proc. Natl. Acad. Sci. U.S.A. accepted.*

Reciprocal Prediction of Multimodal Spectral and Structural Descriptors for Incomplete Data

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Proposing and utilizing machine learning descriptors for chemical property prediction and material screening has become a cutting-edge field of artificial intelligence-enabled chemical research. However, a single descriptor can only include partial features of a chemical research object, resulting in chemical information deficiency and limiting its generalizability. Meanwhile, incomplete data is a common scenario encountered in chemical research, whether the partially incompleteness of multiple descriptors due to sample contamination or the absence of a particular descriptor due to technological difficulties. Herein, we exploit the overlap and redundancy among chemical descriptors to construct an encoder-decoder machine learning training framework that enables reciprocal prediction of multimodal spectral and structural descriptors. After pre-training to endow the model with chemical insights, the multimodal data fusion is implemented in a descriptor-encoded hidden layer. The model's capabilities are validated in the system of CO/NO adsorption on Au/Ag surfaces. The model can not only predict masked data using partially obscured descriptors, but also predict one target descriptor from others. This framework will significantly reduce the model’s dependence on complete physicochemical parameters and improve its multi-target prediction capabilities.

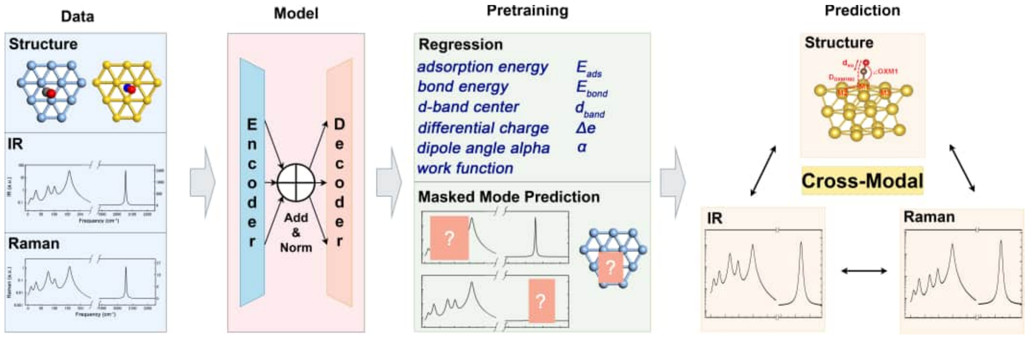

Figure 1. Pipeline of End to End tasks compared with Pretrain Tasks in our work.

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Spectra-Based Clustering of High-Entropy Alloy Catalysts: Improved Insight Over Use of Atomic Structure

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The investigation of material properties based on atomic structure is a commonly used approach. However, in the study of complex systems such as high-entropy alloys, atomic structure not only covers an excessively vast chemical space, but also has an imprecise correspondence to chemical properties. Herein, we present a label-free machine learning (ML) model based on physics-based spectroscopic descriptors to study the catalytic properties of AgAuCuPdPt high-entropy alloy catalysts. Even if the atomic structures of two such alloys are different, these alloys may have similar catalytic properties if their spectral characteristics match closely. One cluster with the strongest CO adsorption exhibited high selectivity and activity for C_{2+} product generation, indicating that the spectra-based ML model can provide deeper chemical insight than one based on atomic structure. Moreover, such a model can be extended to other systems with consistent results, thus demonstrating its transferability and versatility. This not only underscores the potential of spectral analysis in identifying high-performance alloy catalysts, but facilitates the formation of a new spectra-based modeling approach and research theory in materials science.

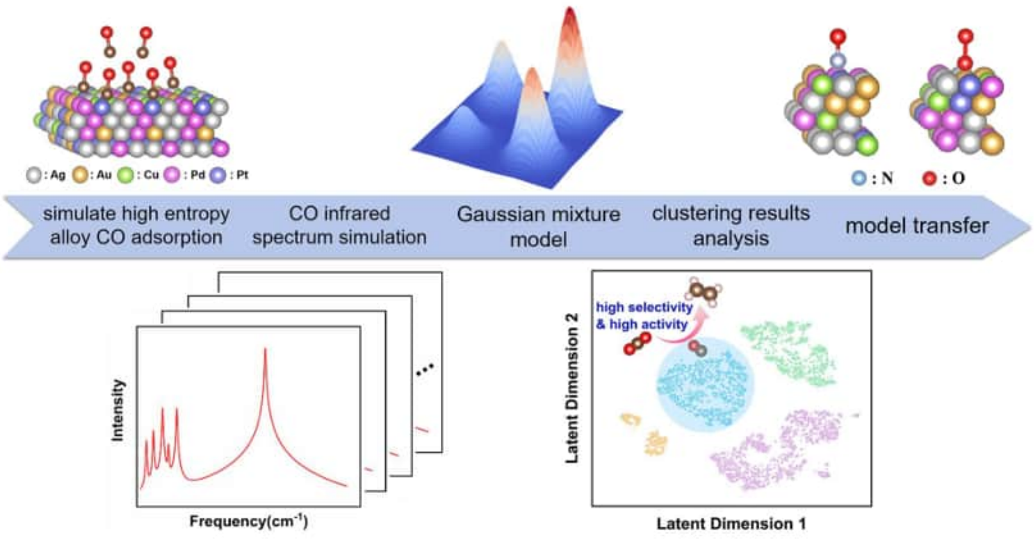

Figure 1. Protocol for using clustering analysis to estimate the catalytic performance of AgAuCuPdPt HEAs using spectroscopic descriptors. Initially, construct various CO adsorption configurations of AgAuCuPdPt HEAs with different compositions and spatial arrangements; subsequently, perform CO infrared spectroscopic DFT calculations for each configuration; next, utilize clustering model analysis to analyze the infrared spectra and the catalytic characteristics of each cluster; finally, transfer the clustering model to NO and O_2 adsorption systems.

A simple approach to rotationally invariant machine learning of a vector quantity

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Unlike with the energy, which is a scalar property, machine learning (ML) predictions of vector or tensor properties poses the additional challenge of achieving proper invariance (covariance) with respect to molecular rotation. For the energy gradients needed in molecular dynamics (MD), this symmetry is automatically fulfilled when taking analytic derivative of the energy, which is a scalar invariant (using properly invariant molecular descriptors). However, if the properties cannot be obtained by differentiation, other appropriate methods should be applied to retain the covariance. There have been several approaches suggested to properly treat this issue. For nonadiabatic couplings and polarizabilities, for example, it was possible to construct virtual quantities from whichthe above tensorial properties are obtained by differentiation and thus guarantee the covariance. Another possible solution is to build the rotational equivariance into the design of a neural network employed in the model. Here we propose a simpler alternative technique, which does not requireconstruction of auxiliary properties or application of special equivariant ML techniques. We suggest a three-step approach, using the molecular tensor of inertia. In the first step, the molecule is rotated using the eigenvectors of this tensor to its principal axes. In the second step, the ML procedure predicts the vector property relative to this orientation, based on a training set where all vector properties were in this same coordinate system. As third step, it remains to transformthe ML estimate of the vector property back to the original orientation.

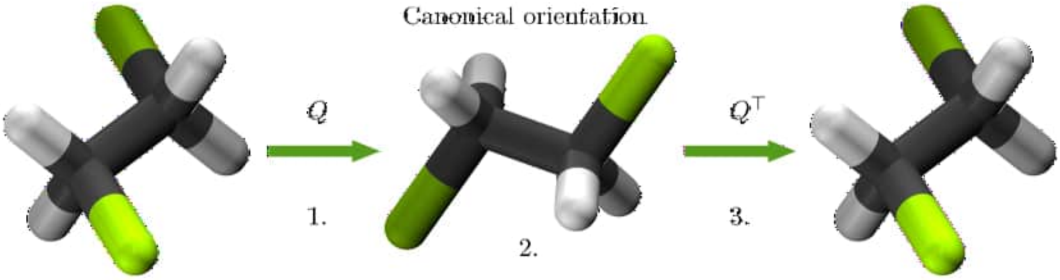

FIG. 1. Proposed RPR approach: 1. rotation of molecule and corresponding properties by $\mathbf{Q}$, 2.prediction by a model trained on molecules rotated into their canonical orientation, 3. backward rotation into the initial orientation $\mathbf{Q}^\top$.

This rotate-predict-rotate (RPR) procedure should thus guarantee proper covariance of a vector property and is trivially extensible also to tensors such as polarizability. The PRP procedure has an advantage that the accurate models can be trained very fast for thousands of molecular configurations which might be beneficial where many trainings are required (e.g., in active learning). We have implemented the RPR technique, using the MLatom and Newton-X programs for ML and MD and performed its assessment on the dipole moment and polarizability along MD trajectories of 1,2-dichloroethane.

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Machine learning photodynamics uncover blocked non-radiative mechanisms in aggregation-induced emission

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Aggregation-induced emission (AIE) is a photophysical phenomenon in which weakly luminescent organic chromophores become strongly luminescent in aggregate. The reduced non-radiative decay in aggregates is often cited as the explanation of AIE. However, the mechanism of competing non-radiative decay pathways is not resolved due to the lack of excited-state structural information in the time-resolved experiments and prohibitively expensive quantum mechanical calculations for photodynamics simulations. We investigated the excited-state dynamics of classic AIE molecules in aggregate, hexaphenylsilole (**HPS**), tetraphenylsilole (**TPS**), and cyclooctatetrathiophene (**COTh**) with a multiscale machine learning accelerated photodynamics approach, integrating neural networks, semiempirical methods, and molecular mechanics. Our simulations predict 263, 5, and 12-fold fluorescence enhancement of **HPS**, **TPS**, and **COTh** in good agreement with the experiments (255, 3, and 12). We identified a shared non-radiative decay mechanism involving πCC torsions in these molecules. These torsions are blocked in aggregate due to intermolecular hindrance between substituents, promoting AIE.

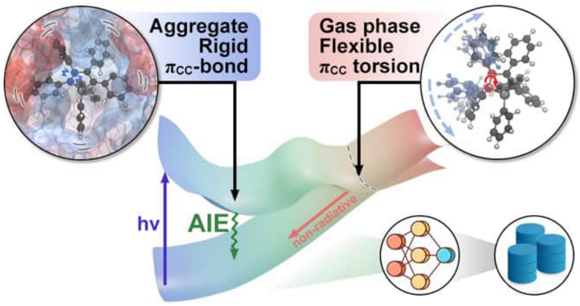

Figure 1. Machine learning photodynamics for aggregates.

Density functional theory and machine learning exploration of disorder in materials

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Disorder phenomena are ubiquitous in emergent functional materials and crucial to materials design. For related problems, conventional atomic-scale computational methods such as using density functional theory (DFT) run into the difficulties of dimensional and combinatorial explosion. My group developed machine learning (ML) methods to integrate DFT data to explore chemical and structural disorder of halide perovskites. For mixed halide alloys $CsPb(I_{1-x}Br_x)_3$ and $CsPb(Br_{1-x}Cl_x)_3$, we calculated thermodynamic state functions based on a traverse DFT exploration over four polymorphs of small model systems, and obtained phase diagrams that semi-quantitatively agree with experiments [1]. To minimize the size effects of computational models, large model systems were required [2] and to this end, our ML model offered accuracy at the DFT level with 10^6 and 10^4 faster for energy and force computations, respectively [3]. We have also studied the disordered structures of $CsPbI_3$ and $CsPbBr_3$ in terms of octahedral tilting, for which the three-dimensional potential energy surfaces were rapidly converged by means of a Bayesian optimization ML scheme. Our results indicate that the high temperature β and α phases of all-inorganic halide perovskites are dynamical average of disordered low-symmetry tilted structures [4].

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Stochastic resolution of identity to CC2 for large systems

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We develop a stochastic variation of the approximate second-order coupled cluster singles and doubles model (sRI-CC2). Using the set of stochastic orbitals, we decouple the crucial 4-index electron repulsion integrals into stochastic resolution of identity. This technique allows a remarkable scaling reduction from $O(N^5)$ to $O(N^3)$, which enables us to calculate the ground state energy as well as the excited state properties for very large systems with nearly thousands of electrons on the coupled cluster level. Additionally, we benchmark the sRI-CC2 method to estimate the stochastic error, and perform calculations on a variety of molecular systems and extended systems. The implementation provides a practical alternative to describe electronic structure properties mainly for large-scaled systems.

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Quantum simulation with cluster embedding strategy for surface chemisty

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Quantum computing offers significant potential for enhancing chemical system simulations. Accurate prediction of absorption energy is crucial for heterogeneous catalysis and requires precise electron wave function simulations. This study introduces a novel hybrid workflow that combines cluster embedding techniques with an active orbital selection method, optimized for near-term quantum computers. Cluster approaches work by placing finite cluster within appropriate embedding environments has been approved high-quality accuracy in predicting absorption energy[1]. As for the selection strategy, starting from HOMO and LUMO, we can automatically pick out orbitals that are related to surface reactions accurately[2]. Applied to the calculation of CO absorption energy on MgO on Q2Chemistry, our approach demonstrates the effectiveness of quantum computing in predicting surface chemical reactions and underscores its practical utility.

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Development of a compact and dynamic ansatz for enhanced quantum efficiency

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Quantum chemistry, characterized by the exponential growth in Hilbert space dimensionality, is a promising area for near-term quantum computing applications. In recent decades, a variety of algorithms have been developed to tackle the complex quantum chemical calculations for many-electron systems. Among these, the Variational Quantum Eigensolver (VQE) has emerged as a leading candidate, attracting considerable attention for its potential to demonstrate quantum advantage with current state-of-the-art devices. However, the effectiveness of VQE can be significantly impacted by the complexity of the ansatz used to represent quantum states. Chemically motivated ansatz, tailored to capture the essential features of molecular systems often involve large and intricate parameter spaces that poses challenges for efficient optimization. To address this, we have developed a chemically motivated dual unitary coupled cluster based ansatz, UiCCSDn [1], which spans the N-electron Hilbert space via rank-one and rank-two parametrization, thus incorporating the high rank correlation effects via reasonably shallow depth quantum circuit. In an attempt to further compactify our ansatz, we developed a first-principle based strategy starting from many-body perturbation theory (MBPT) [2] that dynamically constructs an extremely compact yet highly expressive ansatz that requires zero pre-circuit measurement overhead, thus, safeguarding it from structural alterations due to potential pitfall posed by NISQ architectures.

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Nuclear quantum effects enhance hydrogen evolution reaction on graphene-embedded transition metal atoms

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A growing number of evidence has demonstrated the importance of the nuclear quantum effects (NQEs) in hydrogen evolution reactions, particularly the Tafel step where two hydrogen atoms combine. Meanwhile, recent studies have suggested the formation of two-hydrogen intermediates on a single atomic site in graphene-embedded transition metal catalysts, extending the classic Norskov model for traditional Tafel reactions that assume separate adsorption of hydrogen atoms on active sites [1]. Using the *ab initio* path integral simulations [2], we reveal that NQEs substantially weaken the binding of two-hydrogen intermediates, facilitating their desorption. In addition, nuclear quantum tunneling significantly increases the formation rates of two-hydrogen intermediates across a wide range of temperatures. These findings manifest that NQEs can enhance H_2 production on graphene-embedded transition metal catalysts.

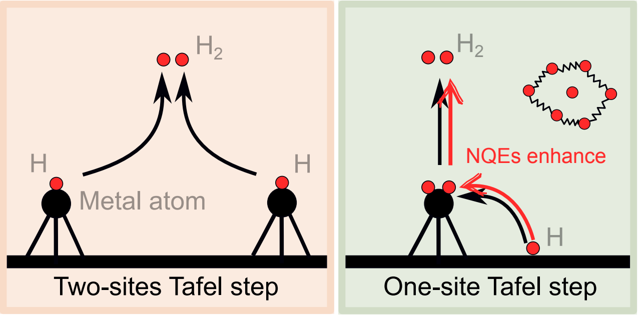

Figure 1. The conventional and novel Tafel reaction.

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Development of quantum embedding computing for quantum chemistry

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Despite recent technological progress, solving the many-electron Schrödinger equation on a quantum computer is still a challenging task, especially if we aim at modeling systems of chemical interest or materials. On the other hand, solving the one-electron Kohn-Sham (KS) equations of density-functional theory (DFT) has been envisioned only very recently as a potential nearest-term application of quantum computers. In the already nontrivial case of quantum DFT for lattice models, which is a promising flavor of DFT for modeling strongly correlated electrons, the major limitation is the absence of a general strategy for designing density (orbital occupation in this case) functionals, which, in this context, are not universal as they depend on the chosen model Hamiltonian. This issue persists and becomes even more critical when turning to the true ab initio quantum chemical Hamiltonian since the latter can be written in any arbitrary (sometimes localized) orbital basis. To overcome these difficulties and to fully benefit from the quantum advantage brought about by quantum computers in the design of accurate energy functionals, we propose to combine expertise in quantum embedding theory (Strasbourg) and quantum algorithms for DFT (Montpellier) in order to provide a general (i.e., applicable to molecules and materials) quantum implementation of a functional-free DFT. To overcome these obstacles and fully leverage the quantum advantage in creating accurate energy functionals, we propose an approach that integrates quantum algorithms with embedding theory in DFT. This would enable a general, material- and molecule-specific quantum implementation of DFT without functional constraints. In this framework, quantum computers would solve both the KS equations for small electron systems and the Schrödinger equation for embedded clusters, capturing local properties as explicit functionals of the density.

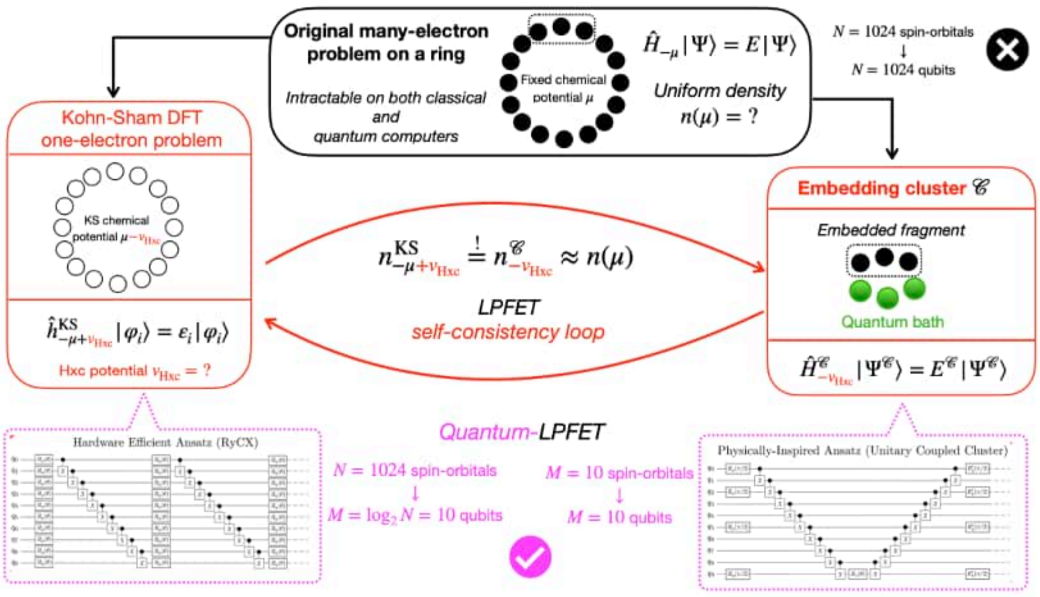

Figure: LPFET and its quantum implementation sketched for a uniform Hubbard lattice.

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Chemoexcited Formation and Radiationless Decay Dynamics of Firefly Chromophore

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Multi-state nonadiabatic dynamics combined with Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT) were performed to investigate the chemoexcitation dynamics of firefly dioxetanone (FDO− in S_0) to oxyluciferin (OxyLH− in S_1) and its subsequent decay dynamics. The formation of oxyluciferin occurs within approximately 100 fs and is primarily controlled by oscillatory CO_2 decarboxylation. Unexpected radiationless decay from oxyluciferin was also observed, facilitated by intramolecular rotation. Simulations under three thermal conditions reveal that higher initial thermal energy enhances the formation of oxyluciferin but also increases radiationless decay by surpassing barriers to the ground state. Conversely, lower thermal energy conditions reduce oxyluciferin formation but suppress radiationless decay. These findings suggest that optimal conditions for higher chemiluminescence quantum yield involve initial high thermal energy to accelerate CO_2 decarboxylation and gradual thermal dissipation to prevent intramolecular rotation of oxyluciferin. This approach could enhance chemiluminescence efficiency beyond the current limit of 40%, offering significant potential for applications in biological imaging and analytical chemistry.

Theoretical study of lanthanide single-ion magnet: electronic structure, magnetic anisotropy and relaxation

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The single-molecule magnet (SMM) performance of a given system is determined by its magnetic relaxation. However, this process could be quite complicated due to the co-existence of various pathways, e.g., Orbach, Raman, QTM. Via *ab initio* electronic structure calculation, we have proposed a concise criterion for high-performance SMM and related theoretical methods in recent years.[1] This criterion is the co-existence of long QTM time τ_{QTM} and high U_{eff}. The computational cost of this criterion can be minimized to one *ab initio* electronic structure calculation for one system.[1] Thus it is easy to apply this criterion to a large number of systems to give a screening of candidates of high-performance SMM[2]. This could largely reduce the burden of subsequent study wherein more accurate but more complicated and computationally expensive method is unavoidable.

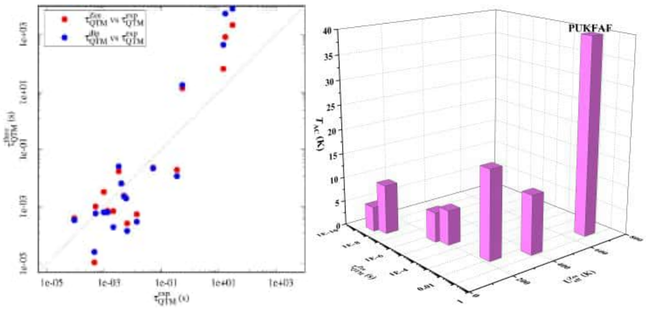

Fig.1 Comparison between theory and experiment.

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The Automated Design of Chemical Reactions Program

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We have developed the Automated Design of Chemical Reaction (ADCR) program (No. 2017SR286149) for automatically exploring diverse reaction pathways. This program is based on the generalized version of the combined molecular dynamics and coordinate driving (MD/CD) method,[1-3] which is cost-effective by exploring low-barrier reaction steps with MD simulations and high-barrier processes with with the modified CD technique. The ADCR program has been applied to multistep reaction pathways for relatively large systems (over 100 atoms), transition-metal containing systems, radical containing systems, single-electron-transfer processes and reactions in condensed phase systems.

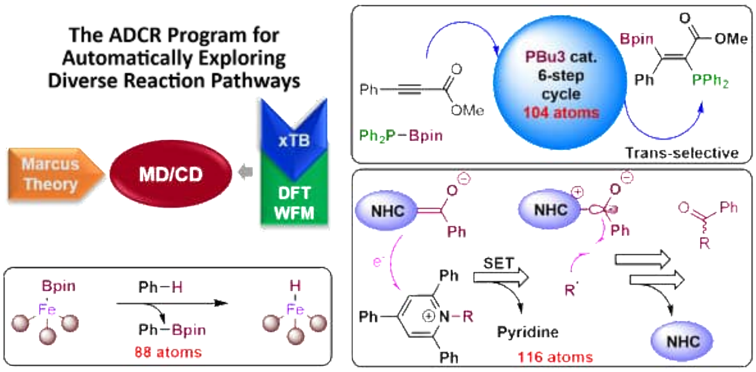

Figure 1. The ADCR program for automatically exploring diverse reaction pathways

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A workflow for reaction datasets construction by layer-based modification modeling process.

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Here we have developed a multi-layer data model for representing chemical structures, where each layer contains information about a meaningful and interchangeable component of the structure, such as catalyst, substrate, substituent or ligand (e.g. Figure 1). The stacking and swapping of layers allows automatic modelling and variable tracking of stable species in a series of reaction pathways. Using recently developed transition state (TS) search algorithms such as iEIP[1], the TS structures on the reaction path can also be automatically searched at lower cost, ultimately allowing the construction of reaction series datasets.

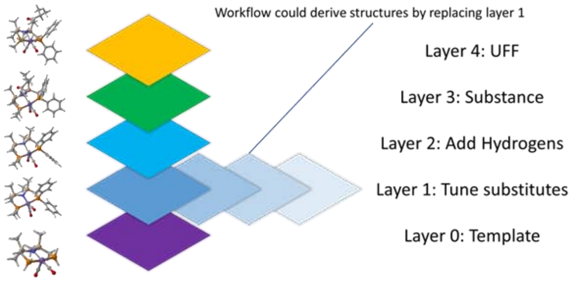

Figure 1. Example of construction related structures in a multi-layer stack.

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Mapping Hydrogen Positions along Proton Transfer Pathway in Organic Crystals by Computational X-ray Spectra

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Understanding proton transfer dynamics is a fundamental issue in chemistry, given its crucial role in numerous chemical and biological processes. Structural information in chemical reactions can provide insights into reaction trajectories, energetic pathways, and the dynamic structural evolution. X-ray diffraction is a widely used technique for structural characterization, while accurately determining the positions of hydrogen poses a significant challenge. However, X-ray spectroscopy, known for typical element- and site-sensitivities, is often used to offer complementary information.

Recently, we have performed a systematic X-ray spectral simulation of the proton transfer process for organic crystals by using the quantum mechanics/molecular mechanics method. Our results provide a continuous spectroscopic mapping, demonstrating the sensitivity of transient XPS/XAS to hydrogen positions and proton transfer. The direct quantum mechanical calculations can make reliable assignments for the resolved peaks of experimental spectra. Further, the exact positions of hydrogen in crystals can be determined by comparison with experiments. Our works[1, 2] highlight the scaled snapshot protocol as an effective theoretical approach for investigating reaction dynamics.

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A Green's-Function-Based Many-Body Perturbation Theory Approach to Electron-Vibration Coupling in Molecular Systems

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Electron-vibration coupling influences the electronic structure. In molecular systems, it changes the HOMO-LUMO gap and results in vibrationally resolved structures in the spectral function. In the 1970s, the Allen-Heine-Cardona (AHC) theory was proposed and widely used in the periodic systems. However, this theory can't provide the spectral function or the vibrationally resolved structures. In this work, we derive a many-body perturbation theory for electron-vibration coupling and implement it in the FHI-aims package. We show the form of the electron-vibration coupling matrix with the atomic orbital basis set and analyze the influences of the AHC approximations in molecular systems. We introduce the electron-vibration self-energy and there is more than one solution of the quasiparticle equation. The solutions correspond to the vibrationally resolved structures of the spectral function one-to-one. Therefore, the quasiparticle energy should be obtained from the spectral function. The spectral function and the photoemission spectroscopy (PES) fit well, which means our method is reasonable. Our work may provide the foundation for future electron-phonon interaction theories in periodic systems.

Reveling the ultrafast energy transfer pathways in energetic materials: Time-dependent and quantum state-resolved

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The β-HMX is a widely used representative high-energy crystal, both experimental and theoretical studies have done a lot of on its energy transfer mechanism over the years in order to utilize its explosive properties and to store and transport it more safely. However, the coupling between the vibrational modes and the ultrafast energy transfer process make it challenge for experimental observation. Therefore, in this work, we determine the energy transfer between different vibrational modes and predict the pump-probe spectra. First, the combined distribution function (CDF) based on normal modals coordinates is analyzed to find the strongly coupled vibrational modes, and then the pump-probe spectra are calculated. The complex vibrational spectral regime can be divided into two parts, probe molecules (clusters) and the environment, so obtaining the correct time-dependent transitions, including environmental perturbations, is an important challenge. The local quantum vibration embedding (LQVE) [1]method, which combines molecular quantum vibrations and molecular dynamics with perturbation theory to introduce dynamic environmental effects more comprehensively, has been successfully applied to the simulation of several systems, and has obvious advantages in terms of accuracy and transportability. Classical molecular dynamics is used to describe the dynamical effects in the β-HMX crystal system, considering the quantum effects of atomic nuclei, while quantum mechanics is used to describe the vibrations of the probe molecules. PODVR saves the cost while accomplishing an efficient description of the vibrational state. The structures in each step of the dynamical trajectory are processed with degrees of freedom using our self-developed molecular substitution algorithm, which in turn computes the instantaneous properties of the molecule (e.g., instantaneous vibrational frequency, transition polarization rate, etc.) using the quantum-mechanical approach. Calculating the pump-detection spectra, the coupling of multiple vibrational modes and multiple quantum states can be handled to further accurately describe the energy transfer between important modes.

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Second-order Møller–Plesset perturbation theory with pair natural orbitals for periodic systems

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To this day, the toolset for describing electron correlation in periodic systems remains DFT-centred. Despite its low cost and strengths, DFT lacks systematic improvability and is known to have difficulties with noncovalent interactions such as dispersion. Periodic methods are still largely missing the tremendous advancements that molecular quantum chemistry has experienced in the past two decades to reduce the steep polynomial scaling encountered in second-order Møller–Plesset perturbation theory (MP2) and coupled-cluster methods.

The Turbomole package is uniquely placed to address this. A periodic LCAO Hartree-Fock method is already available within the *riper* module [1], providing the necessary infrastructure for computing crystal orbital coefficients in terms of Bloch atomic orbitals for a set of *k*-points. Efficient molecular pair natural orbital (PNO) methods for MP2 and CCSD(T) are available in the *pnoccsd* module [2] and can readily be extended to a periodic setting.

This contribution will discuss recent developments to implement a periodic LCAO PNO-MP2 method in the Turbomole environment. We outline the general framework of the PNO-MP2 approach, and highlight some key adaptions for the periodic scheme, such as the generation of localised occupied Wannier functions, the imposition of periodic boundary conditions on virtual orbitals, the use of translational invariance to reduce cost, and the treatment of the slow converging lattice sum of the Coulomb integrals. Preliminary results on non-conducting systems are presented.

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Equation-of-Motion Block-Correlated Coupled Cluster Method for Excited Electronic States of Strongly Correlated Systems

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An equation-of-motion block-correlated coupled cluster method based on the generalized valence bond wave function (EOM-GVB-BCCC)[1] is proposed to describe low-lying excited states for strongly correlated systems. The EOM-GVB-BCCC2b method with up to two-pair correlation has been implemented and tested for a few strongly correlated systems. For a water hexamer with stretched O−H bonds, which is beyond the capability of the CASSCF method, EOM-GVB-BCCC2b provides very close results as the density matrix renormalization group (DMRG). For four conjugated diradical species with triplet ground states, we found that their vertical S−T gaps from EOM-GVB-BCCC2b are also quite consistent with the DMRG results. This new method is expected to be a promising theoretical tool for describing the low-lying excited states of strongly correlated systems with large active spaces.

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Toward A Systematic and High-Precision Ab Initio Framework for Metallic Solids

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In the era of data-driven science, ab initio simulations using wave function methods for periodic solids continue to hold great promise due to their ability to provide highly accurate data, enhancing the predictive power of quantum chemistry across diverse research fields, such as heterogeneous catalysis, in silico materials design for batteries, and quantum materials. These methods are powerful because they systematically approach the exact solution for the electronic structure of materials. In practice, the main challenge lies in the steep computational cost, particularly when striving for accurate results that require convergence with respect to the complete basis set limit, the thermodynamic limit, and the exact electron correlation limit.

In this work, we describe our efforts to develop a framework and software ecosystem aimed at achieving convergence in these three dimensions. To better address electron correlation beyond the density functional approximation, we use multi-level theories within embedding spirit that gradually approach the accuracy of high-level methods. Additionally, we develop algorithms that leverage graphical processing units (GPUs) to accelerate computationally intensive tasks. We apply this framework to the CO puzzle, which involves the CO adsorption on metallic surfaces, where conventional methods like density functional theory fail to provide even qualitative accuracy, and random phase approximation struggles with quantitative precision.

The truncation schemes for unitary coupled-cluster based polarization propagator theory

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The unitary coupled-cluster (UCC) based polarization propagator theory (PPT) is a novel Hermitian quantum chemical method for calculating excited states. Since there are infinite terms of the expansion of UCC similarity transformed Hamiltonian, it is crucial for developing an accurate and efficient truncation scheme for practical application of UCC-based method. A third-order UCC-PPT (UCC3) approach [1] based on perturbation theory and a quadratic UCC-PPT (qUCCSD) approach [2] based on commutator truncation were developed and implemented. The computational performance of these two methods was assessed by carrying out benchmark calculations using QUEST database [3]. A systematical accuracy improvement of the commutator truncation approach (qUCCSD) relative to perturbation approach (UCC3) has been observed. Followed by previous commutator truncation approaches, the extend version of qUCCSD (eqUCCSD) is proposed. The details and numerical results of this method are discussed and analyzed in this work.

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A moiety-based charge-transfer decomposition for exploring the charge-transfer character and exciton binding energies in dye-sensitized solar cells

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This study presents a dual-focused approach to advancing electronic structure calculations and their applications in photovoltaics. We developed a graphical user interface (GUI) for PyBEST [1], a modern electronic-structure software package, using Electron.js. This GUI enhances PyBEST's accessibility, enabling non-programmers to utilize its capabilities effectively. Furthermore, we employed PyBEST to investigate eight carbazole-based dyes for dye-sensitized solar cell (DSSC) applications. Using paired Coupled Cluster Doubles (pCCD) [2] and Equation-of-Motion (EOM) [3,4] methods, we analyzed the electronic properties crucial for DSSC performance. Our findings reveal significant bridge-to-acceptor charge transfer and dominant local bridge excitations across all dyes. We also calculated key electronic properties including ionization potentials, electron affinities, and exciton binding energies. This research demonstrates the potential of computational approaches in guiding the development of new materials for photovoltaic applications. By combining an accessible software interface with advanced quantum chemical methods, we provide a promising pathway for accelerating the design and optimization of organic dyes for DSSCs.

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DC-MP2-PBC: Fast and accurate quantum chemical calculation for large-scale periodic systems

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It remains a challenge to elucidate the functional manifestations of doped amorphous materials using electronic structure calculations. When employing *ab initio* quantum chemical methods, which can systematically improve accuracy and have typically been applied to isolated systems, it is necessary to construct large-scale cluster models to mitigate "edge effect." Similarly, when using methods from condensed matter physics that treat periodic systems with DFT, constructing large-scale periodic models capable of adequately describing the amorphous structure is essential. Since there are few DFT methods that offer the same level of systematic improvement as *ab initio* methods, the development of a large-scale periodic boundary condition (PBC) calculation method based on *ab initio* methods has been highly desired.

We have developed the divide-and-conquer (DC) Hartree-Fock (HF) and post-HF methods as accurate fragmentation-based calculation methods for large-scale isolated systems [1,2]. In this study, we extended the DC-HF and MP2 methods to periodic systems and developed the DC-HF/MP2-PBC program. This program leverages the features of the DC method to solve periodic systems using a real-space Gaussian basis (Figure). This approach is similar to fragment molecular orbital (FMO) calculations with PBC [3]. We applied this program to amorphous materials to attempt to elucidate their functional manifestations from their electronic states.

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Figure. Subsystem construction for PBC and calculation time.

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Unveiling the Local Structure of Liquid Water via X-ray Spectroscopy Simulations Employing Multiconfigurational Wave Function Theory

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X-ray absorption spectroscopy (XAS) has emerged as a powerful tool for investigating the electronic and structural properties of molecules. By manipulating photon energy to excite core electrons, it offers element-specific insights into materials and finds broad applications in various fields of chemistry, such as catalysis, materials science, and biochemistry.1,2 Within this framework, the XAS spectra of water have been widely investigated, serving as a paradigmatic example. The oxygen K-edge XAS spectrum of liquid water displays prominent peaks at specific energy values: the pre-edge (~535 eV), main edge (~538 eV), and post-edge (~541 eV), corresponding to confined intramolecular excitons, excitons localized within the coordination shell, and the delocalization spanning distant water molecules, respectively.3 Furthermore, the hydrogen bonding network has been identified as a key player in shaping and modulating the energy levels present in the XAS spectrum of water, yielding valuable insights into its intricate fine structure.4,5 This relationship is still not fully understood although it is indispensable for obtaining structural information about water systems. In an effort to improve this description, we develop a computational protocol that combines molecular dynamics (MD) simulations and accurate multireference (MR) calculations to calculate the XAS spectra of water, with the goal of enhancing our understanding of the absorption spectrum-water structure relationship and improving the description of the XAS spectra of water.

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U≡C Triple Bonds in Fullerene Compounds

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Despite decades of efforts, the actinide−carbon triple bond has remained an elusive target, defying synthesis in any isolable compound. Herein, we report the successful synthesis of uranium−carbon triple bonds in carbide-bridged bimetallic [U≡C−Ce] units encapsulated inside the fullerene cages of C_{72} and C_{78}. The molecular structures of UCCe@C_{2n} reveal very short uranium−carbon bonds of 1.921(6) and 1.930(6) Å, with the metals existing in their highest oxidation states of +6 and +4 for uranium and cerium, respectively. Quantum-chemical studies further demonstrate that the C_{2n} cages are crucial for stabilizing the [$U^{VI}{\equiv}C{-}Ce^{IV}$] units through covalent and coordinative interactions. This work offers a new fundamental understanding of the elusive uranium−carbon triple bond and informs the design of complexes with similar bonding motifs, opening up new possibilities for creating distinctive molecular compounds and materials.

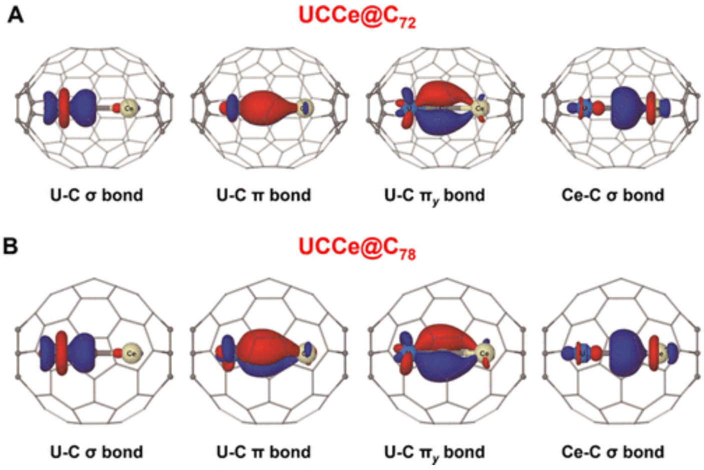

Figure 1. Four NLMOs on the endohedral UCCe unit.

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Design Strategy of MR-TADF Materials with Tunable Stokes Shift and Narrow Spectra Band: Through-Space Conjugation

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Organic fluorescent emitters with narrowband red (R)-green (G)-blue (B) emissions are highly desirable for high-resolution organic light-emitting diode (OLED) display technology. However, according to Franck-Condon principle, simultaneously achieving narrow spectra band and large Stokes Shift is contradictory [1]. Noncovalent through-space conjugation (TSC) is gradually proved as an important strategy for enhancing optoelectronic properties by modulating molecular conformations [2]. Herein, we reveal that its nature is two π-π orbital interactions, the strength depends on the molecular structure and the degree of orbital overlap between the conjugated groups. The descriptor A based on structural parameters is proposed to characterize the TSC strength and to establish the relationship between strength and spectra property. More importantly, we propose the TSC strategy to achieve the synergistic regulation of spectra bandwidth and Stokes shift, theoretically predict the multi-resonance thermally activated delayed fluorescence (MR-TADF) systems for narrow spectra band with larger Stokes shift, break through the traditional cognition that the narrow spectra band are bound to have small Stokes shift. This strategy solves the scientific problems of color purity and self-absorption, narrow spectra band, and the difficulty of the exciton particle number inversion.

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Million-atom molecular dynamics simulations on the splitting mechanism of Ni particles within the anode of solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) are promising for their high-power generation efficiency without the need for noble metal catalysts. However, Ni/YSZ anodes degrade in humidified hydrogen environments, primarily due to the splitting of Ni particles, which disrupts the electronic conductive path. It is therefore important to suppress the splitting in humidified hydrogen environment. Experiments are insufficient to reveal the precise dynamics and mechanisms of the splitting at atomic scale. Meanwhile, reactive molecular dynamics (MD) simulations allow intuitive observation of the behavior of Ni particles on the YSZ surfaces. This study aims to elucidate the splitting mechanism of Ni particles in a humidified hydrogen environment (50%H_2-50%H_2O) by reactive MD simulations, utilizing models at million-atom scale (Fig. 1). Our findings show that Ni particles predominantly split near their edges on the YSZ surface. The mechanism is as follows: OH terminations formed by water dissociation on the Ni surface reduce its surface tension, leading to a lower contact angle between Ni and YSZ. As the Ni flattens, its edges become thin and structurally unstable, which induces the splitting. The details will be discussed during the presentation.

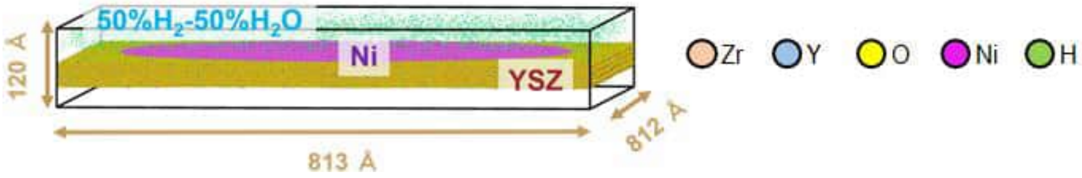

Fig. 1. Million-atom Ni/YSZ model in humidified hydrogen environment.

Relativistic effects in ultrafast light induced spectroscopy

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We present fundamental insights on pure electron dynamics captured by pump–probe attosecond transient spectroscopic techniques, within the realms of real–time time-dependent density functional theory [1-4]. We incorporate both scalar and spin-orbit relativistic effects variationally using modern atomic mean-field eXact two-component (amfX2C) Hamiltonian [4]. We address how this technique records the signature of the transient dynamics triggered by the pump pulse imprinted onto the molecular response to probe pulse, including effects of additional degrees of freedom (pump pulse features and pump–probe time delay) absent in conventional spectroscopy.

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Time evolving matrix product operator (TEMPO) method in a non-diagonal basis set based on derivative of the path integral expression

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The time-evolving matrix product operator (TEMPO) method is a powerful tool for simulating open system quantum dynamics. Typically, it is used in problems with diagonal system-bath coupling, where analytical expressions for discretized influence functional are available. In this work, we aim to address issues related to off-diagonal coupling by extending the TEMPO algorithm to accommodate arbitrary basis sets. The proposed approach is based on computing the derivative of the discretized path integral expression when increasing one time step, which yields an equation of motion valid for non-diagonal basis set. The generalized path integral is then obtained by integrating the resulting differential equation. Applicability of the new method is then tested by simulating one- and two- qubit systems coupled to both Z-type and X-type baths. We also compare the results with our 2DMPS method[1].

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MC23: A New Meta-GGA On-Top Functional for Hybrid Multiconfiguration Pair-Density Functional Theory with Improved Accuracy

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The development of Kohn-Sham density functional theory (KS-DFT) using density functional approximations (DFAs) has transformed the field of quantum chemistry. However, because KS-DFAs use spin densities ($\rho_{\alpha/\beta}$) and other quantities, such as spin density gradients ($g_{\alpha/\beta}$) and kinetic energy densities ($\tau_{\alpha/\beta}$), that are computed from a single Slater determinant, the accuracy of modern KS-DFAs is usually lower on strongly correlated systems than their accuracy on weakly correlated systems, where strongly correlated systems are those whose wave function requires more than one Slater determinant for a qualitatively correct description.

A decade ago, multiconfiguration pair-density functional theory[1] (MC-PDFT) was proposed to improve the treatment of strongly correlated systems. The functionals of MC-PDFT use the spin-summed electronic density (ρ) and the on-top pair density (Π) to obtain the nonclassical energies. Therefore, the density functionals in MC-PDFT are called on-top functionals. Current on-top functionals are translation of existing KS-DFAs. For example, tPBE in MC-PDFT is PBE[2] evaluated with effective spin densities ($\rho_{\alpha/\beta}^{\text{eff}}$) and effective spin density gradients ($g_{\alpha/\beta}^{\text{eff}}$) computed from ρ and Π. Until now, the on-top functionals have not been optimized for MC-PDFT. The goal of the present work is to optimize an on-top functional, and as part of this work we propose a way to include kinetic energy density in an on-top functional. We optimized an on-top functional based on the M06-L functional form together with a fraction of the wave-function energy. The new on-top functional, called MC23, is optimized against a diverse set of databases. Our results show that MC23 demonstrates good accuracy on both strongly and weakly correlated systems. In contrast, recently developed KS-DFAs have similar accuracies as MC23 on weakly correlated systems, but are less accurate on strongly correlated systems. Our work on MC23 shows that MC-PDFT is a more robust framework than KS-DFT in treating both weakly and strongly correlated systems equally accurately, and we recommend MC23 for future MC-PDFT calculations.

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Rare event kinetics in complex systems with Milestoning

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Many important physical and biochemical processes in biomacromolecular systems occur on time scales greater than milliseconds and hence are not easily captured through brute-force molecular dynamics (MD) simulations. As such, they are called rare events. However, their outcomes can significantly impact the functionalities of molecular systems. Therefore, we desire an accurate and efficient atomically MD method to simulate the rare event process of biomacromolecular systems. We latest proposed local passage time weighted Milestoning (LPT-M) is an accurate and efficient method for rare event kinetics calculations. Due to the high degree of freedom of biomacromolecular systems, not only are Milestoning networks derived from MD simulations growing in number, as also getting increasingly complex. The increased complexity of the networks makes more difficult to analyze the system qualitative and understand of the underlying mechanism. To address this challenge, simplifying the network structure while preserving the kinetic information becomes crucial. We propose a reduced analysis algorithm for the Milestoning network, which contains three steps. First, nodes (milestones) in the network are grouped into clusters based on metastability of the system. Here we introduce a composite matrix to make our clustering method is applicable not only to time-reversible networks but also to non-reversible networks generated from practical simulations, owing to statistical fluctuations. Second, finding the core set of clusters by free energy calculation, a reduced and equivalent network consisting of only core sets of clusters as nodes is established. Finally, transition pathways are analyzed in the reduced network based on the Transition Path Theory to find important pathways and bottlenecks. We hope apply Milestoning more widely to the simulation and mechanism analysis of biomacromolecule systems.

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How Transcription Factor NF-κB RelA Recognize a Central Base Pair: Computational Insights into Transient Interactions

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Nuclear factor kappa B (NF-κB) transcription factors (TFs) are crucial for gene regulation by binding to κB DNA elements with conserved flanking sequences surrounding a degenerate central region. The RelA homodimer, a wide-expressed NF-κB TF, exhibits varying affinities determined by the base pair at the central position of DNA, with A or T conferring tenfold higher affinity than G or C. However, crystal structures offer limited insights into the underlying mechanisms for these affinity differences. Through extensive molecular dynamics (MD) simulations and machine learning, we uncovered two key residues of RelA, R187 and R124, and their distinct dynamic behaviors. R187 interacts with major groove-bound residues, critically influencing their base contacts through differential transient states; R124 enhances base interactions by favored transient insertion into the minor groove in A-κB over G-κB. Both residues displayed selective transient interactions that orchestrated a complex interplay among DNA-interacting residues, which are subsequently validated by mutagenesis studies. These findings deepen our understanding of the intricate mechanisms governing the selective binding of NF-κB to κB DNA, highlighting the role of MD simulations in unraveling the dynamic details of TF-DNA interactions.

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Accurate Carbohydrate-Binding Site Prediction

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As the most abundant organic substances in nature, carbohydrates are essential for life. Understanding how carbohydrates regulate proteins in the physiological and pathological processes presents opportunities to address crucial biological problems and develop new therapeutics. However, the diversity and complexity of carbohydrates pose a challenge in experimentally identifying the sites where carbohydrates bind to and act on proteins. Here, we introduce a deep learning model, DeepGlycanSite, capable of accurately predicting carbohydrate-binding sites on a given protein structure. Incorporating geometric and evolutionary features of proteins into a deep equivariant graph neural network with the transformer architecture, DeepGlycanSite remarkably outperforms previous state-of-the-art methods (Table 1) and effectively predicts binding sites for diverse carbohydrates [1]. Integrating with a mutagenesis study, DeepGlycanSite has been employed to reveal the nucleotide-sugar-recognition site of several important G-protein coupled receptors [1, 2]. It also provides insights for the design of carbohydrate-detection biological nanopore [3, 4]. These findings demonstrate DeepGlycanSite is invaluable for carbohydrate-binding site prediction and could provide insights into molecular mechanisms underlying carbohydrate-regulation of therapeutically important proteins.

Table 1. Comparing DeepGlycanSite with previous binding site predictors on the independent dataset.

Method	MCC	Precision	BA
StackCBPred	0.018	0.052	0.525
Fpocket	0.191	0.194	0.617
SiteMap	0.227	0.201	0.717
DeepPocket	0.288	0.292	0.760
PeSTo	0.336	0.235	0.815
DeepGlycanSite (ours)	0.625	0.631	0.829

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Probing the Orientation and Membrane Permeation of Rhodamine Voltage Reporters through Molecular Dynamics and Free Energy Calculations

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The transmembrane potential of plasma membranes and membrane-bound organelles plays a crucial role in cellular functions such as signal transduction, ATP synthesis, and homeostasis. Rhodamine Voltage Reporters (RhoVRs), which operate based on photoinduced electron transfer (PeT) mechanisms, are non-invasive, highly sensitive, and can detect rapid voltage changes, with some specifically targeting the inner mitochondrial membrane. We conducted extensive molecular dynamics simulations and free energy calculations to investigate the orientation of three RhoVRs, which significantly influences their sensitivity and membrane permeation behavior. Our results indicate that the relative positioning of the polarized tail is crucial for enhancing alignment with the membrane normal, thereby maximizing sensitivity. Additionally, free energy calculations across different membrane systems identified an extra energy barrier for RhoVR1 compared to SPIRIT RhoVR1, explaining their distinct cellular localizations. The divide-and-conquer approach in the free energy calculation elucidates the underlying physicochemical properties. These insights guide the design of more sensitive voltage dyes and enhance our understanding of their cellular localization mechanisms.

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CO_2 to Methanol Conversion on Cu/ZnO Catalyst: Unveiling the Role of Catalyst Architecture and Binding Affinity

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In heterogeneous catalysis, transition metal nanoparticles (NPs) are usually supported on oxides that effectively prevent NP agglomeration, modify NP shapes and electronic structures, ultimately bolstering catalyst stability and activity. However, the interaction between NPs and oxides is still not clear.[1] ZnO, for instance, serves as a prevalent substrate for NP catalysts in various industrial processes such as methane steam reforming and methanol synthesis. A longstanding debate persists regarding the structure of active sites for CO_2 hydrogenation to methanol on Cu/ZnO catalysts. [2]

In our recent studies, we first developed reliable models for Cu NPs supported on the ZnO $(10\bar{1}0)$ with realistic active site structures by systematic screening of different size and shapes of NPs using interatomic potentials (IP) and density functional theory (DFT) calculations. The electronic analysis of the interface between Cu NPs and ZnO $(10\bar{1}0)$ revealed that Cu atoms donate electrons to ZnO, decreasing the charge on adjacent Zn cations and notably changing the d-bands of interface Cu atoms. Based on the most thermodynamically stable Cu/ZnO model obtained, we explained the reaction mechanism for CO_2 hydrogenation to methanol through a combination of density functional theory (DFT) calculations and microkinetic simulations. Focusing on the HCOO pathway for methanol synthesis, we identified different key intermediate steps that govern the reaction mechanism for our chosen catalysts (Cu/ZnO, CuZn alloy and ZnO/Cu {111} models). Notably, our models revealed a substantial disparity in CO_2 binding affinity among the three catalysts, with the Cu/ZnO displaying the highest binding energy, exceeding others by more than 0.6 eV, a pivotal factor in the free energy profile (Figure 1). The microkinetic analysis further indicated that the product selectivity for CH_3OH is notably elevated in the case of Cu/ZnO underscoring the significance of the interface model in methanol synthesis.

In summary, our study provides valuable insights into the atomic-level understanding of the CO_2 hydrogenation to methanol on Cu/Zn catalysts, offering a foundation for enhanced catalyst design.

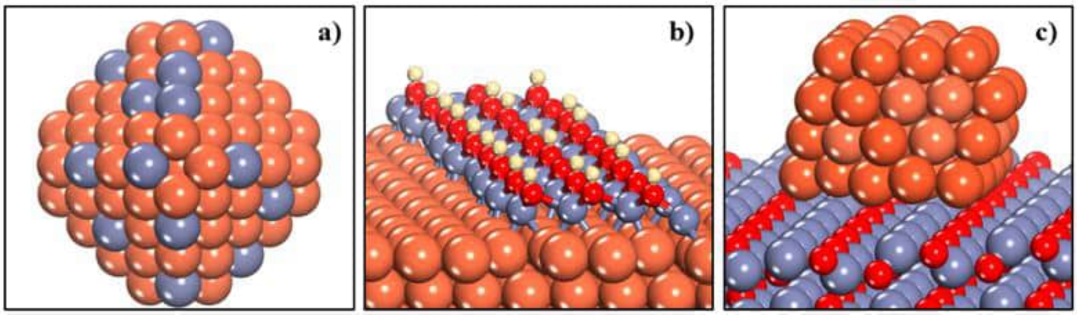

Figure 1. Lateral and top views of three different structural models: a) Cu-Zn alloy; b) ZnO/Cu; c) Cu/ZnO

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Tailoring active-site spacing of single-atom catalyst for CH_4-to-CH_3OH conversion: Co_1/UiO-66 MOF as an exemplary model

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Developing catalysts for mild and selective oxidation of methane to methanol (CH_4-to-CH_3OH) is a challenging yet crucial endeavor for the industry. In this study, we propose a strategy to enhance the selective methane oxidation reaction, focusing on the crucial step of metal-oxo active site formation. Our findings demonstrate that optimizing the spacing between active metal sites can facilitate efficient charge transfer from the metal sites to O_2, thereby kinetically enhancing O_2 activation and leading to the formation of highly reactive O (oxo) species capable of activating the methane C-H bond. Through the screening of different metals at varying metal site spacings, we find that the Co single atom exhibits favorable properties and performance, characterized by the duality of low O_2 activation energy and the radical character of the formed metal-oxo species. Utilizing a Co single-atom catalyst dispersed on UiO-66 MOF as a probe catalyst, we have showcased the potential of tailoring the active site spacing to enhance their activity and selectivity towards methane oxidation to methanol. Notably, the newly designed catalyst surpasses the activity of a known catalyst, achieving a observable turnover frequency (TOF) (>1 $s^{-1}site^{-1)}$ at 350K, while also enhancing its selectivity by inhibiting continuous methane dehydrogenation. This strategic approach could provide valuable insights for further exploration of MOF-supported single-atom catalysts or other support morphologies for the selective oxidation of CH_4-to-CH_3OH with excellent activity in the gas phase. Moreover, it can be extended to other chemical reactions, including the reduction of nitrogen to ammonia.

Inverted Region in Electrochemical Reduction of CO_2 Induced by Potential-Dependent Pauli Repulsion

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Electrochemical CO_2 reduction reaction (eCO_2RR) is of great significance to energy and environmental engineering, while fundamental questions remain regarding its mechanisms. Herein, we formulate a fundamental understanding of the interplay between the applied potential (U) and kinetics of CO_2 activation in eCO_2RR on Cu surfaces. We find that the nature of the CO_2 activation mechanism in eCO_2RR varies with U, and it is the sequential electron–proton transfer (SEPT) mechanism dominant at the working U but switched to the concerted proton–electron transfer (CPET) mechanism at highly negative U. We then identify that the barrier of the electron-transfer step in the SEPT mechanism exhibits an inverted region as U decreases, which originates from the rapidly rising Pauli repulsion in the physisorption of CO_2 with decreasing U. We further demonstrate catalyst designs that effectively suppress the adverse effect of Pauli repulsion. This fundamental understanding may be general for the electrochemical reduction reactions of closed-shell molecules.

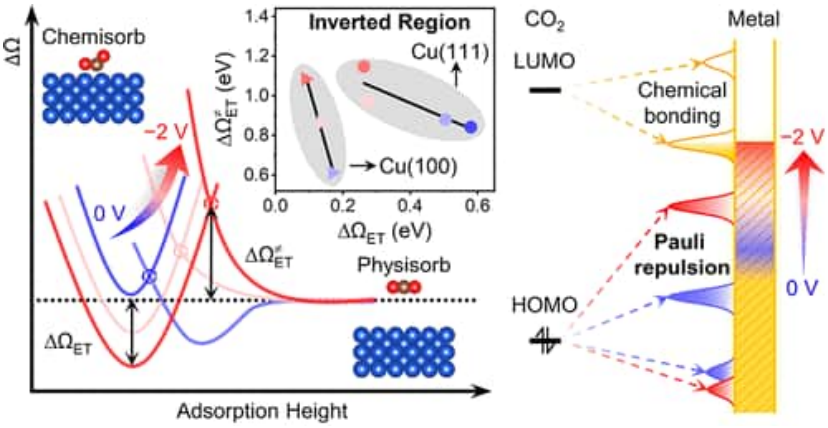

Figure 1. The origin of the inverted region in the CO_2 activation in eCO_2RR.

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Effective Screening Descriptors of Metal−Organic Framework Supported Single-Atom Catalysts for Electrochemical CO_2 Reduction Reactions

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Metal−organic framework-supported single-atom catalysts (SACs@MOF) show considerable promise in CO_2 reduction reactions (CO_2RR). However, efficiently screening and designing optimal catalysts is hindered by the lack of effective descriptors for encoding the complex chemical microenvironments in SAC@MOF systems. Herein, through combining an intuition-guided dimensionality reduction strategy with machine learning (ML), we identified critical descriptors based on atomic features and the SAC’s constrained coordination geometry, which capture the effects of complex chemical microenvironments on electrochemical CO_2RR activity and selectivity for UiO-66supported SACs. With these descriptors, accurate ML models were developed to predict the limiting potentials for producing HCOOH, CO, and CH_4/CH_3OH on 48 SACs@UiO-66-X (X = H, NH_2, and Br). Moreover, the transferability of the developed descriptors and ML models was demonstrated on 48 additional systems with X = CH_3, OH, and NO_2. The accuracy of the predicted activity trends for specific SACs combined with different linker groups and the selectivity of the top-performing catalysts were validated through additional DFT calculations.

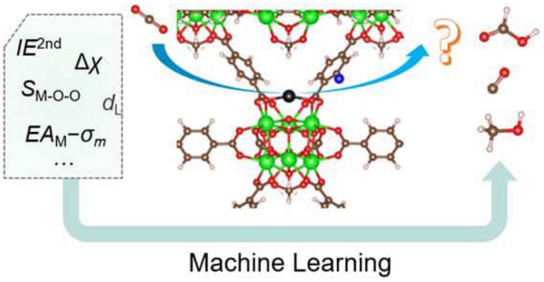

Figure 1. Descriptors for electrochemical CO_2RR on SACs@MOF.

Towards systematic initiations of minimum energy path calculations

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The exploration of reaction pathways lies at the heart of understanding chemical processes, with applications ranging from catalysis to drug design. A reaction path in its fundamental form describes the rearrangement of atoms between reactant and product state along a connected set of structures, providing insight into the kinetics of the reaction. With the advancement of computational hardware and quantum chemical methods in the recent years, computational and data-driven reaction network discovery has become accessible, revolutionizing the way chemical space is explored, thus accelerating the development of novel molecules and materials [1,2,3]. However, at the heart of this endeavor still lies the efficient generation of minimum energy paths (MEP), which are often needed *a priori* as feedstock for data driven methods. It has been shown that the MEP generated by common use gradient-based methods such as the Nudge Elastic Band (NEB)[4] or string[5] method heavily rely on the initial path and the coordinate space chosen[6].

In this regard we present a systematic and broad comparison of representations used in MEP generators, as well as a diverse dataset of benchmark reactions for reaction-exploration algorithms. Our dataset shows large chemical diversity, containing molecules with up to 21 heavy (non-hydrogen) atoms from the reaction space spanned by C, H, O, N, S, P, B, F, Cl and Br. By including larger and chemically more diverse molecules than previously established datasets [7,8] we provide an opportunity to test the robustness and predictive capabilities of established methodologies.

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A theoretical study on the asymmetric site of CO_2 hydrogenation to methanol on Cu-based catalysts

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Density functional theory (DFT) has greatly enhanced our knowledge of methanol synthesis via CO_2 hydrogenation on Cu-based catalysts. Nevertheless, differences in catalytic performance with varying metal dopants have obstructed the creation of universal catalytic principle. In this reaction, the activation of carbon dioxide is critical, and asymmetric sites play a key role in the activation of carbon dioxide. To explore the characteristics of these activation sites, a series of Cu-O-X (X=Zr, Zn, Ce, etc.) sites were established and a series of descriptors were obtained. With these descriptors, the activation capacity of CO_2 can be predicted by the adsorption energy of the species. This method enhances our understanding of the relationship between energy and linear expressions on copper-based substrates. Additionally, the universal linear criterion can be applied to other catalytic systems, with the goal of identifying potential catalysts that are both highly efficient and cost-effective.

CO_2 electroreduction to CO on ultrasmall Ag nanoparticles supported on polymeric carbon nitride (PCN).

The electrochemical reduction of CO_2 (CO_2RR) is a desirable reaction to generate feedstock for producing valuable chemicals from greenhouse gases. Many metal catalysts can reduce CO_2 electrochemically; however, only a few metal catalysts can selectively reduce CO_2 to CO. The $Ag_4/PCNH_{x-4}$ catalyst is realised by substituting Ag single atoms with H atoms, weakly bonded to the regularly separated nitrogen anchoring groups in the PCN support. This stimulates the formation of ultrasmall Ag nanoparticles under thermodynamically controlled conditions. The two mechanisms considered for this process are Oswalt Ripening and Particle Migration and Coalescence. The barriers for the mechanisms were calculated and referenced with graphene substrate to comprehend the effect of PCN. Structural stability of possible $Ag_4/PCNH_{x-4}$ structures in electrochemical conditions is explored concerning the potential aggregation of Ag atoms to form ultrasmall nanoparticles. Different sizes of truncated octahedral Ag nanoparticles ranging from 0.8 to 2.1 nm are employed to determine the nanostructuring effect of the activity and selectivity of various sites in CO_2RR and competing hydrogen evolution reactions (HER). The stability of the considered nanoparticles is analysed through their excess surface energies. The binding Gibbs Free energies of the different reactants and intermediates are evaluated using Density Functional Theory (DFT) to calculate the different reaction step energies for CO_2RR and HER mechanisms on various positions of considered Ag nanoparticles and $Ag_4/PCNH_{x-4}$ structure. In summary, the theoretical study found low coordinating sites on ultra-small Ag nanoparticles to selectively catalyse CO_2 for CO reduction while impairing the competing HER activity compared to high coordinating atoms and Ag (111) single crystal surface.

The oxidation of CO on step interfaces between ZnO deposits and metal supports

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The catalytic oxidation of CO can be used to treat exhaust emissions from combustion engines. Noble metals can be good catalysts at high temperatures, but their surfaces are easily covered by CO, which stops the reaction and hinders their application. As alternative catalysts, composites of oxides and metals have been highlighted due to their tunable structures and properties [1]. Here, the CO oxidation mechanism involving O atoms at the step oxide/metal interface (Figure 1) will be discussed for ZnO combined with metal supports: Pd, Pt, Cu, Ag, and Au. Density functional theory calculations leading to reaction profiles and microkinetic simulations revealed that all composites studied have better catalytic properties than bare Pt and Pd under 600 K. Catalytic inactivation from side reactions with H_2O is also studied to motivate a discussion about the challenges in designing the best possible system to treat exhaust gases from combustion engines.

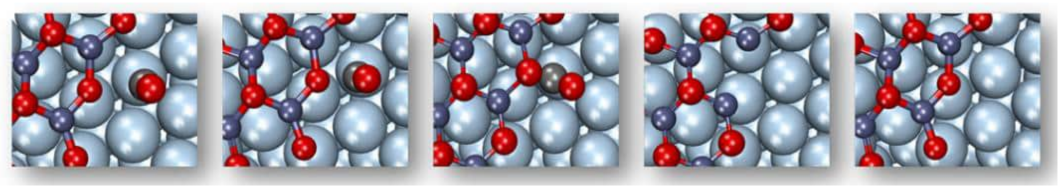

Figure 1. Most important structures formed during the oxidation of CO through lattice O atoms on interfacial oxide/metal sites.

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Small molecule activation by uranium and group 6 metal complexes: a theoretical study

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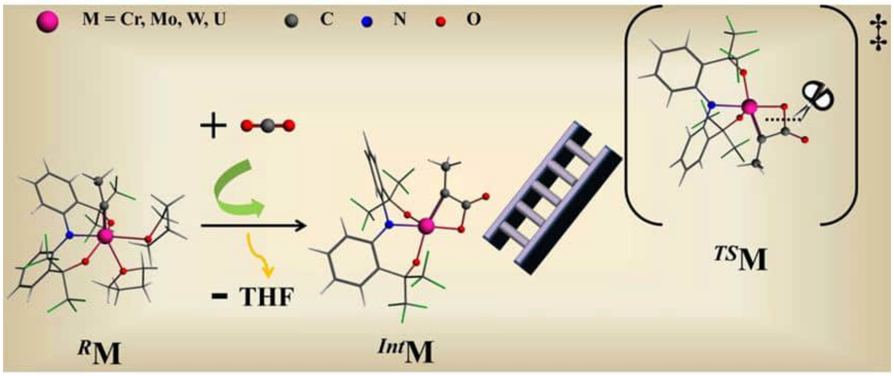
Designing novel catalysts is essential for the efficient conversion of metal alkylidyne into metal oxo ketene complexes in the presence of CO_2, which to some extent resolves the environmental concerns of the ever-increasing carbon emission.[1-5] In this regard, a series of metal alkylidyne complexes, [***b-ONO***]$M\equiv CCH_3(THF)_2$ ([***b-ONO***] = $\{(C_6H_4[C(CF_3)_2O])_2N\}^{3-}$; M = Cr, Mo, W and U) have been comprehensively studied by relativistic density functional theory calculations. The calculated thermodynamics and kinetics unravel that the tungsten complex is capable of catalyzing the CO_2 cleavage reaction, agreeing with the experimental findings for its analogue. Interestingly, the uranium complex shows superior catalytic performance because of the associated considerably lower energy barrier and larger reaction rate constant. The M≡C moiety in the complexes turns out to be the active site for the [2+2] cyclic addition. In contrast, complexes of Cr and Mo could not offer good catalytic performance. Along the reaction coordinate, the M-C (M = Cr, Mo, W and U) bond regularly transforms from triple to double to single bond; concomitantly, the newly-formed M-O in the product is identified as triple-bond character. The catalytic reactions have been extensively explained and addressed by geometric/electronic structures as well as bonding analyses.



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Explicitly Density-Dependent Noncollinear and Nonlocal Exchange-Correlation Functional

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In Kohn-Sham density functional theory (DFT), the exact exchange-correlation functional should be both noncollinear in spin space and nonlocal in real space. However, most existing functionals do not simultaneously possess noncollinear and nonlocal forms. In this work, we apply a multicollinear approach [1] to the nonlocal weighted spin density approximation (WSDA) [2] functional to construct the first explicitly density-dependent functional that is both noncollinear and nonlocal. Preliminary tests show this functional correctly reproduces the collinear limit and is sensitive to the relative orientations of spin magnetization in separated subsystems.

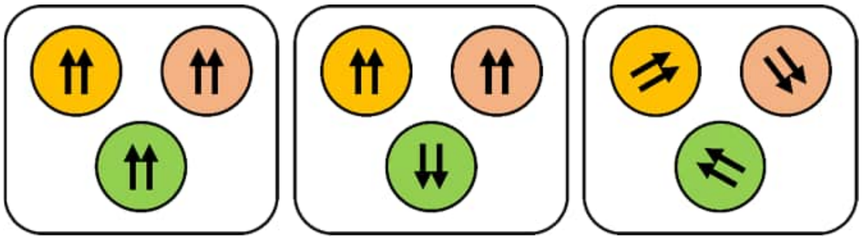

Figure 1. The left and middle subfigures represent collinear systems with separated varying spin polarizations, which traditional local and semilocal functionals cannot distinguish. The right subfigure shows a noncollinear system that collinear functionals cannot handle.

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A tuning method for range-separated hybrid functionals based on Charge Transfer density-based indexes

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Many literature surveys show that global hybrid functionals, while being successful in predicting several properties, may fail to correctly predict the energy of excited states with relevant charge-transfer (CT) character. Range separated hybrids and especially optimally tuned RSH have been proven to provide an efficient solution to this problem.

Here we propose a novel procedure to optimize the range separation parameter in a system adaptable and computationally inexpensive way, correlating it to the estimated CT length [1] computed for excited states. as range separation distance.

We tested the accuracy of the so obtained range separated making use of the PBE exchange and correlation counterpart (LC-PBE0*). [2-3]

This functional has been tested for intra- and inter- molecular CT excited states, showing high accuracy in the prediction of both CT and Local Excited states, encouraging for its wider application to other chemically relevant compounds and devices.

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Energetic Information from Information-Theoretic Approach in Density Functional Theory as Quantitative Measures of Physicochemical Properties

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The Hohenberg-Kohn theorem of density functional theory (DFT) stipulates that energy is a universal functional of electron density in the ground state, so energy can be thought of having encoded essential information for the density. Based on this, we recently proposed to quantify energetic information within the framework of information-theoretic approach (ITA) of DFT (*J. Chem. Phys*. **2022**, *157*, 101103). In this study, we systematically apply energetic information to a variety of chemical phenomena to validate the use of energetic information as quantitative measures of physicochemical properties. To that end, we employed six ITA quantities such as Shannon entropy and Fisher information for five energetic densities, yielding twenty-six viable energetic information quantities. Then, they are applied to correlate with physicochemical properties of molecular systems, including chemical bonding, conformational stability, intermolecular interactions, acidity, aromaticity, cooperativity, electrophilicity, nucleophilicity, and reactivity. Our results show that different quantities of energetic information often behave differently for different properties but a few of them, such as Shannon entropy of the total kinetic energy density and information gain of the Pauli energy density, stand out and strongly correlate with several properties across different categories of molecular systems. These results suggest that they can be employed as quantitative measures of physicochemical properties. This work not only enriches the body of our knowledge about the relationship between energy and information, but also provides scores of newly introduced explicit density functionals to quantify physicochemical properties, which can serve as robust features for building machine learning models in future studies.

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Exact Properties of Multi-State Density Functional Theory

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With good balance between computational accuracy and efficiency, density functional theory (DFT) has been an indispensable tool for scientists in chemistry, physics and materials. However, DFT has been insufficient in describing general excited states and systems with strong electronic correlation. Therefore, it is a demanding challenge in theoretical chemistry to develop a universal approach based on DFT for simulation of excited states. We report a rigorous formulation of multi-state density functional theory (MSDFT) that treats ground and excited states on an equal footing [1]. We establish the fundamental theorems of MSDFT. First, we prove the existence of a Hamiltonian matrix functional $\mathcal{H}[D]$ of the multi-state matrix density D(r) in the N-dimensional Hilbert subspace V^N. Then, we establish the variational principle of MSDFT, which states that variational minimization of the subspace energy, equal to the trace of $\mathcal{H}[D]$, with respect to the matrix density D(r) yields both the exact eigen-energies and densities of the N lowest eigenstates. Next, we show that the Hamiltonian matrix functional $\mathcal{H}[D]$ can be explicitly constructed by introducing a minimal active space (MAS), accompanied by the correlation matrix functional $\mathcal{E}^c[D]$, which accounts for correlation effects outside the MAS [2-3]. Based on the fundamental theorems of MSDFT, we further show that there exists a fundamental symmetry for the matrix functionals, namely the subspace invariance property, being a necessary condition for state interaction [4]. Derived from the subspace invariance property, we obtain a set of exact relationships between matrix elements of the correlation matrix functional. These exact relationships lead to a fundamental theorem to the analytical structure of $\mathcal{E}^c[D]$. That is, given the correlation functional for a single state in the N-dimensional subspace, all elements of the correlation matrix functional for the entire subspace are uniquely determined [5]. Approximated methods based on the framework of MSDFT have been successfully applied to simulate excited-state properties of systems with weak and strong correlation. These findings reveal the intricate structure of electronic correlation within the Hilbert subspace of lowest eigenstates and suggest a promising direction for efficient simulation of excited states.

$$\begin{pmatrix} \rho_1(r) & \cdots & \cdots & D_{1N}(r) \\ \vdots & \rho_A(r) & \vdots & \vdots \\ \vdots & D_{BA}(r) & \ddots & \vdots \\ D_{N1}(r) & \cdots & \cdots & \rho_N(r) \end{pmatrix} \Rightarrow \begin{pmatrix} \mathcal{H}_{11}[\mathbf{D}] & \cdots & \cdots & \mathcal{H}_{1N}[\mathbf{D}] \\ \vdots & \mathcal{H}_{AA}[\mathbf{D}] & \vdots & \vdots \\ \vdots & \mathcal{H}_{BA}[\mathbf{D}] & \ddots & \vdots \\ \mathcal{H}_{N1}[\mathbf{D}] & \cdots & \cdots & \mathcal{H}_{NN}[\mathbf{D}] \end{pmatrix}$$

$$\mathbf{D}(\mathrm{r}) \qquad \Rightarrow \qquad \mathcal{H}[\mathbf{D}]$$

$$E_{\mathrm{MS}}[\mathbf{D}^{\mathbf{o}}] = \min_{\mathbf{D}(r)}\{\mathrm{tr}(\mathbf{S}^{-1}\mathcal{H}[\mathbf{D}])\}$$

Figure 1. The Hamiltonian matrix functional $\mathcal{H}[D]$ and variational principle of MSDFT.

Keywords: Density Functional Theory; Excited States;

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Exploring the range-separation schemes in the range-separated hybrid functionals

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Most range-separated hybrid functionals use simple functions like the error function to complete the range-separation. Here we present our primary results on exploring the best range-separation functions. Starting with the CAM-B3LYP functional and fitting the atomization energies in the G3 dataset, we find the mean-absolute error can be reduced from 4.8 kcal/mol to 2.5 kcal/mol by using a new range-separation function. Meanwhile, the optimized range-separation function is not monotonic, we are still trying to understand the physics behind.

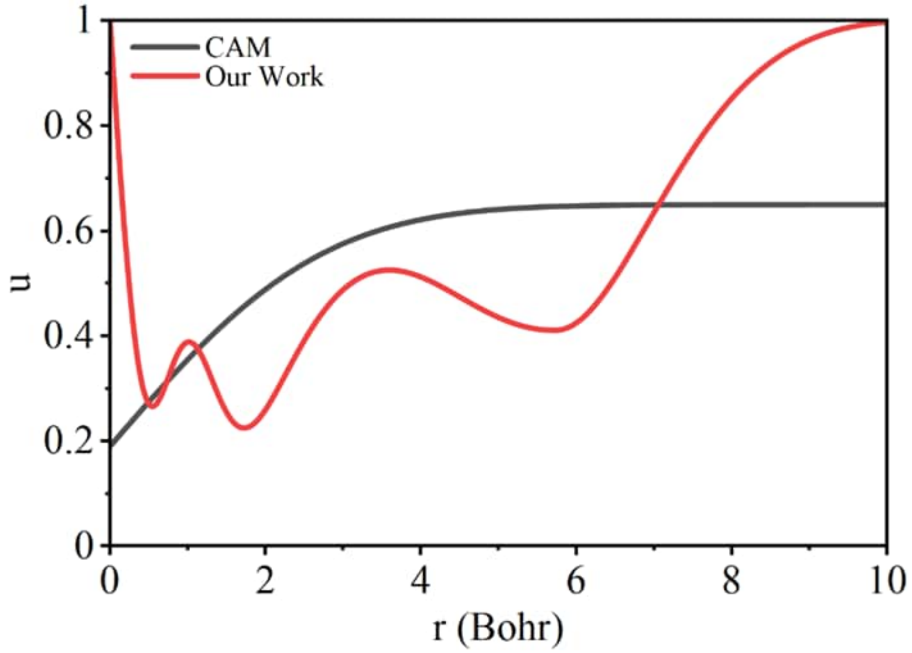

Figure 1. Range-separation functions of the CAM-B3LYP functional and our realization.

Towards consistent projection-based wavefunction in density functional theory embedding

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Projection-based embedding [1,2] is a method which provides a robost and simple framework to combine wavefunction methods with density functional theory (DFT). The full system is partitioned into the subsystem of interest, which is treated with a high-level method such as wavefunction-based electron correlation methods and its environment that is treated at the DFT level. The partition and assignment of orbital space is usually based on orbital localization. However, it may be difficult to keep the orbital space consistent when scanning potential energy surfaces (PES). In this work, we show that the PES discontinuities can be eliminated by a singular-value-decomposition-based approach which guarantees that the orbital spaces of two adjacent geometries have maximum similarity.

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Comparison of solvent electrostatic potential and improvement proposal for polarizable continuum model

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The polarizable continuum model (PCM) is one of the low-cost and widely used solvation models. This model has been pointed out that stabilization by solvation is underestimated when a solute has a charge [1]. We focused on the electrostatic interaction term as the cause and compared the reaction field with other models. Here, we show the reaction field distributions formed by water solvent around a neutral phenol. In DFT/PCM and 3D-RISM-SCF, the solute was treated as B3LYP/6-31+G(d,p). In MD and 3D-RISM, solute and solvent were treated with GAFF and RESP charges. For the water parameter, ε=78 was adopted for PCM, and TIP3P was adopted for others. The temperature is 300K.

Figure 1 shows that the characteristics of the PCM reaction field are very gentle and a weak reproduction of the orientation of hydrogen bonds involving a solute's proton. Improvements would be better focused on these characteristics. Results for other solutes will be presented at the poster session.

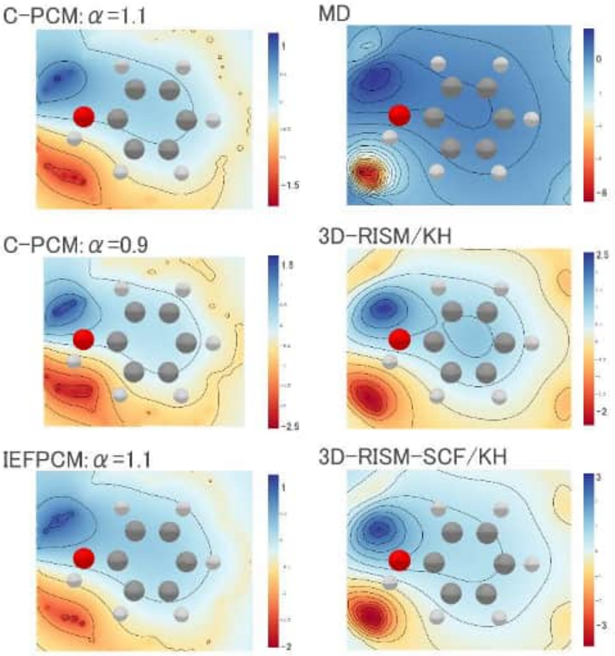

Figure 1. Reaction field distribution by water solvent around a phenol.

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Role of electronic polarization in the primary charge-transfer states of the purple bacteria reaction center: A polarizable QM/MM study with the integral-exact direct reaction field method

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A hybrid quantum mechanical (QM)/molecular mechanical (MM) study with the integral-exact direct reaction field (IEDRF),[1][2] polarizable embedding scheme was performed on the purple bacteria reaction center of $Rhodobacter\ sphaeroides$ in order to investigate how polarization induced in the protein matrix helps to stabilize the primary charge-transfer (CT) states relative to the exciton states of the special pair. The protein environment is represented by point charges and induced dipoles that are coupled to the QM region via the integral-exact direct reaction field Hamiltonian, which can simultaneously describe differential solvation of multiple electronic states of different polarities. Treating the special pair, $P = P_L P_M$, and bacteriopheophytin, H_L and H_M, quantum mechanically, we compare excitation energies computed at the ωPBEh time-dependent density functional theory level for CT states along the active and inactive branches. Thermal fluctuations on the electronic-state energies are included by extracting snapshots from a molecular dynamics trajectory.

We find that the polarization in the protein is largely dictated by the secondary structure, with induced dipoles pointing along the axes of α-helices. The relaxation of dipoles on the excited state provides similar stabilization of both branches; however, the ground-state polarization, captured by IEDRF, screens $P^+H_L^-$ more than $P^+H_M^-$ and is thus key to directing the CT towards the active branch. The different ground-state dielectric environment of the two branches is confirmed by computing relative local fields at key carbonyl probes.[3] With IEDRF embedding, we find the local fields to be in near quantitative agreement with the interpretations of recent vibrational Stark-effect experiments, while the agreement is diminished for electrostatically embedded QM/MM calculations. These results caution against QM/MM calculations with electrostatic embedding alone, because CT states in a rigid, dense protein matrix are mostly stabilized by the fast electronic polarization of the surrounding medium.

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Application of Quantum Embedding Theory on Lanthanide-based Materials

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First-principles studies of the optical properties of lanthanide-based materials suffer from severe errors when mean-field approximation is applied, because of the strongly correlated essence of open-shell f-electrons[1]. Among various theoretical methods that have been developed for strongly correlated systems, MCSCF has played a particularly important role as it provides a systematic approach to static correlation, but a direct application of those approaches to extended systems like solids and surfaces becomes computationally prohibitive due to the exponential scaling. Density matrix embedding theory (DMET), which combines low-level and high-level correlated quantum chemistry methods, provides a systematic framework to reduce the computational cost [2-4]. In this work, we present two efficient quantum embedding approaches, starting from either periodic ROHF calculations or ab initio model potential (AIMP) to approximate the periodic systems with non-periodic clusters, and then combine them with DMET. The complete active space self-consistent field and subsequent state interaction treatment of spin–orbit coupling (CASSI-SO) is further applied to the embedded cluster space to describe the strongly correlated active center[5].

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Excitonic energy transfer under strong coupling from a semi-classical surface hopping perspective

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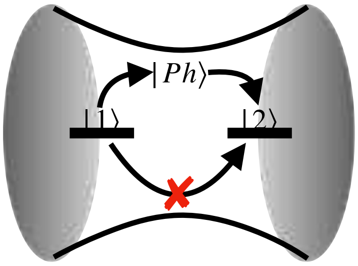
Strong coupling between molecule and radiation mode inside a cavity leads to formation of hybrid entity, polaritons which exhibits characteristics of both molecule and radiation. Experimentally polaritons have been found to change rate of reactions by orders of magnitude. In this work, we have benchmarked surface hopping method for electronic strong coupling inside a cavity. The comparison of surface hopping method is done with numerically exact HEOM method for a model system for a broad range of parameters. Surface hopping method can capture both on and off resonance effects. We also have looked at parameters that can increase or decrease the rate of energy transfer and surface hopping method captures it well.



Two site coupled with each other as well as through photon mode inside a cavity. Exciton energy transfer is preferred by coupling through the photon mode

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Ab-initio study on the effect of dipolar spin-spin interactions in singlet fission

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Interactions between triplet pair states are known to play a key role in important chemical processes. An example is singlet fission (SF), a photo-induced multiple exciton generation mechanism in which a singlet excited state transforms into a pair of triplet excitons [1]. Electron paramagnetic resonance experiments have provided evidence that this process involves the participation of singlet $|^{1}(TT)\rangle$ and quintet $|^{5}(TT)\rangle$ coupled triplet pair states [2,3,4]. In this contribution, we employ *ab-initio* multi-reference perturbation theory techniques to investigate the effect of dipolar spin-spin interactions on the SF dynamics. For this, we have investigated a series of modified pentacene dimers where the pentacene-like moieties are covalently bonded to a phenylene linker in ortho, meta and para positions shown to undergo intramolecular SF [5]. Our results provide insight into the spin mixing in these systems, in particular regarding the effect of the inter-triplet relative orientation and the strength of the zero-field splitting on the fate of the coupled triplet pair state in SF.

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Radiosensitizing potential of halo-uracils via low-energy electrons: A simulation study

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Halouracils (XUs) have long been explored as potential radiosensitizers: substances that increase the sensitivity of cancer cells to radiation and thus enhance the effectiveness of radiotherapy. Despite longstanding interests, the initial events of XU radiosensitization remain unclear. In particular, while it is understood that following radiolysis, XUs form transient negative ions through interactions with radiation-generated secondary electrons, leading to halide dissociation and the formation of reactive uracil radicals, fundamental questions about this process remain: What is the electronic state formed after the electron attaches? Is internal conversion (IC) involved? What is the role of solvation? Previous theoretical studies have largely focused on gas-phase XU.[1] To make contact with time-resolved spectroscopy experiments carried out in the aqueous phase,[2] we used our recently developed FlexiBLE QM/MM boundary method,[3] combined with a quasi-particle DFT-based electronic-structure method,[4] and the ab initio multiple spawning excited-state dynamics simulation package[5] to simulate the dynamics of bromouracil following electron attachment. Our results suggest two competing pathways: (I) rapid IC from a π_2^* to a σ^* state leading to Br^- dissociation, and (II) non-dissociative IC to a nonreactive π_1^* state, impeded by a small barrier. This suggests a design principle of elevating excited-state potential barrier heights to minimize non-dissociative IC for improved nucleobase-derived radiosensitizers.

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Describing Nuclear Quantum Effects in Coupled Nuclear-Electron Dynamics at Gas-Metal Surface: A Ring Polymer Molecular Dynamics Extension to Electronic Friction

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Molecular dynamics with electronic friction (MDEF) is a well-established simulation method that has been widely applied to study nonadiabatic effects near metal surfaces. However, MDEF treats the nuclear degrees of freedom completely classically, hence the nuclear quantum effects (NQEs) are completely missing. Here, we present how a simple Ring Polymer Molecular Dynamics (RPMD) extension to MDEF, denoted as EF-RPMD, which can efficiently incorporate the NQEs. Employing a centroid mode friction approach, we significantly improved both the equilibrium / steady state properties as well as the electron transfer dynamics. Notably, EF-RPMD accurately predicts the transition of the two dominant electron transfer channels from barrier crossing to tunneling as temperature decreases. Finally, EF-RPMD can recover qualitatively correct steady-state properties, such as the I-V curve, in the presence of a chemical potential bias. We expect that our method will be very useful to study nonadiabatic dynamics near metal surfaces when nuclear quantum effects become essential.

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First-principles demonstration of nonadiabatic thouless pumping of electrons in a molecular system

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Nonadiabatic Thouless pumping of electrons is studied in the framework of topological Floquet engineering, particularly focused on how atomistic changes to chemical moieties of *trans*-polyacetylene control the emergence of the Floquet topological phase. We employ real-time time-dependent density functional theory to investigate the extent to which the topological invariant, winding number, is impacted by molecular-level changes. In particular, we consider several substitutions to trans-polyacetylene to study different types of effects on the electronic structure including mesomeric effect, inductive effect, and electron conjugation effect. As previously demonstrated in our work [1], we use the maximally localized Wannier functions to relate the winding number to the valence bond description by expressing the topological pumping as the transport dynamics of the localized Wannier functions. We further exploit the gauge invariance of the quantum dynamics with respect to the single-particle orbital representation by using the so-called dynamical transition orbitals [2], and it offers a minimal description of the quantum dynamics in terms of the particle-hole excitation. This allows us to analyze the topological pumping in terms of the equilibrium molecular orbital description, and the pumping of electrons can be understood as a cyclic transition among the C-C bonding and antibonding orbitals. Having connected the topological invariant to chemically intuitive concepts, we rationalize how atomistic changes impact the emergence of the Floquet topological phase and it opens up an opportunity for systematic and intuitive molecular-level engineering of chemical systems for such an exotic topological phase.

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A Grid-based Gauge-Invariant Non-Perturbative Solution of the Schrodinger Equation for Electrons and Nuclei in Strong Magnetic Fields

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Strong magnetic fields which compete with the Coulomb forces in atoms and molecules affect structure, energetics, degeneracies, symmetries and dynamics of both the electrons and the nuclei. The complex and coupled nature of the interactions make it difficult to intuitively understand the response of the system to the external field. A direct non-perturbative solution of the Schrödinger equation for the system and field is thus undertaken where fields have been incorporated in the grid-based Hamiltonian ensuring gauge invariance for all grid sizes. Validation of the implemented method and computation of diatomic rovibrational spectra is undertaken.

Non-adiabatic molecular dynamics on ultrafast relaxation of *ortho*-nitrophenol upon photoexcitation

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Ortho-nitrophenol (o-NP) is a proto-typical molecule that exhibits excited state intramolecular proton transfer (ESIPT) between adjacent substituents. It is also a potential source of nitrous acid, contributing to the photochemical generation of OH radicals in the atmosphere. Time-resolved experiments [1,2] in the last decade suggested ultrafast deactivation through internal conversion (IC) in a sub-picosecond timescale. On the other hand, the experimental observation of a long-lived excited state [1] also indicates the possibility of intersystem crossing (ISC). Non-adiabatic molecular dynamics studies [3,4,5] have suggested different mechanisms; however, they are not sufficient to explain the experimental facts [1] supposed to include both IC and ISC. Therefore, the underlying mechanism of ultrafast relaxation dynamics of o-NP remains unknown, which is addressed in the present study.

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Theoretical Study of the Spin Transition Processes of Molecular Systems

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Transitions between different spin states provide an effective regulation strategy in excited-state chemistry, where the interactions between electronic spin and other angular momentums, such as electronic orbitals, electron spins, and nuclear spins, lead spin transitions in molecular systems from forbidden to controllable. In this talk, I will show some theoretical studies of excited-state spin dynamics, developing effective computational methods and applying them to photo-induced applications such as energy transfer and photodynamic therapy. The calculation of spin-changing processes, including intersystem crossing, intermolecular spin exchange, and spin dynamics of radical ion pairs from photo-induced charge transfer, will be presented.

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Phonon-Mediated Ultrafast Energy- and Momentum-Resolved Hole Dynamics in Monolayer Black Phosphorus

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Electron-phonon scattering plays a crucial role in determining the electronic, transport, optical, and thermal properties of materials. Here, we employ a non-Markovian stochastic Schrödinger equation (NMSSE) in momentum space [1], together with ab initio calculations for energy bands and electron-phonon interactions, to reveal the phonon-mediated ultrafast hole relaxation dynamics in the valance bands of monolayer black phosphorus. Our numerical simulations show that the hole can initially remain in the high-energy valence bands for more than 100 fs due to the weak interband scatterings, and its energy relaxation follows single-exponential decay towards the valence band maximum after scattering into low-energy valance bands. The total relaxation time for hole is much longer than that of electron in conduction band. This suggests that harnessing the excess energy of holes may be more effective than that of electrons [2]. Compared to the semiclassical Boltzmann equation based on a hopping model, the NMSSE highlights the persistence of quantum coherence for a long time, which significantly impacts the relaxation dynamics. These findings complement the understanding of hot carrier relaxation dynamics in two-dimensional materials and may offer novel insights into harnessing hole energy in photocatalysis.

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Large-Scale Nonadiabatic Dynamics Study of Doping Process within PbSe Quantum Dots

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Colloidal quantum dots (QDs) are widely used in electronic and optoelectronic devices. As major application scenarios, laser media, solar cells, as well as light-emitting diodes, make serious demands on the appearance of free carriers within QDs. Therefore, a thorough understanding of the doping mechanism is essential for the precise fabrication and stable maintenance of the doped QDs.

To investigate the intrinsic mechanism underlying the p-doping process involving QDs and oxidants, an all-atom Holstein Hamiltonian for lead selenide QDs is constructed, incorporating effects such as anharmonic nuclear potential energy, nonlinear electron-phonon coupling, and non-local electronic coupling, with all parameters derived from *ab initio* electronic structure calculations. Utilizing the Crossing-Corrected Global Flux Surface Hopping (CC-GFSH) method within a mixed quantum-classical dynamics framework, we successfully simulate the doping process in QDs containing thousands of electronic energy levels. We then calculated the electron entropy using the von Neumann definition, allowing us to analyze the energy and entropy driving forces throughout the dynamics. Based on this electron-level analysis, we successfully achieved stable p-doped QDs by eliminating hole trappers on the QD surface.

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Multi-scale Modeling of Hydroxyl Radical Reactions with Isoprene in the Gas Phase and at the Air-Water Interface

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The hydroxyl radical (·OH) plays a crucial role in the atmospheric chemistry of organic compounds, significantly impacting air pollution and climate. Its reactions with isoprene, the most abundant atmospheric volatile organic compound (VOC), lead to the formation of ozone and secondary organic aerosols (SOAs) through a series of oxidation products. While these reactions are ubiquitous, the mechanisms, particularly at the air-water interface[1], remain poorly understood.

To delineate the key physical and chemical aspects of ·OH and isoprene reactions in gas phase and at the air-water interface on the molecular scale, we utilize a multi-scale modeling strategy. This approach utilizes quantum mechanical (QM) data from relatively small systems as a reference to parametrize more efficient empirical valence bond (EVB) models[2], enabling simulations of these ·OH and isoprene reactions for bigger sizes and longer time scales in various chemical environments. Our work will provide insights into the molecular details that are difficult to obtain from experiment, and also provide useful information for other thermodynamic models commonly used by atmospheric scientists.

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Ab Initio Investigation of the Features of $Sr_3Ti_3(BO_6)_2$

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In this study, we build upon previous experimental work on the novel material $Sr_3Ti_3(BO_6)_2$, as reported in the article [1] by conducting first-principles calculations using Density Functional Theory (DFT). Our computational study aimed to validate and extend the experimental findings, focusing on both structural and electronic properties.

Firstly, we calculated the hkl indices and compared our results to the experimental data, finding a discrepancy of only 3-5%, which falls within the acceptable range of DFT accuracy. This suggests that our theoretical model accurately represents the material's crystallography. Additionally, we investigated the mechanical properties, providing further insight into the material's potential applications.

Moreover, we computed the electronic band structure, revealing a band gap that aligns well with the experimental observations, thereby confirming the material's semiconducting nature. We also constructed a convex hull at 0 K, which indicates that $Sr_3Ti_3(BO_6)_2$ is metastable under these conditions.

Our results suggest that $Sr_3Ti_3(BO_6)_2$ is a metastable material with potential applicability in optical applications, making it a promising candidate for further exploration in this field.

ISTCP 2024

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Study of the influence of the grain boundary structure on the properties of CsPbBr3 perovskite

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The paper presents the theoretical description of the grain boundary in CsPbBr3 perovskite. The calculation of the mean squared displacement shown in Figure 1a indicates the migration of Br atoms. Using the values of the displacement of atoms relative to the initial position as a parameter of the mobility of atoms, we obtain the value of the slope of the straight MSD from different values of the selection parameter for highly mobile atoms (atoms of the boundary) (Figure 1b). Thus, we define the boundary condition for determining GB atoms. Figure 1c shows a diagram of the structure with the indicated displacements of GB atoms under the boundary condition. Note that GB atoms tend to shift along the grain boundary.

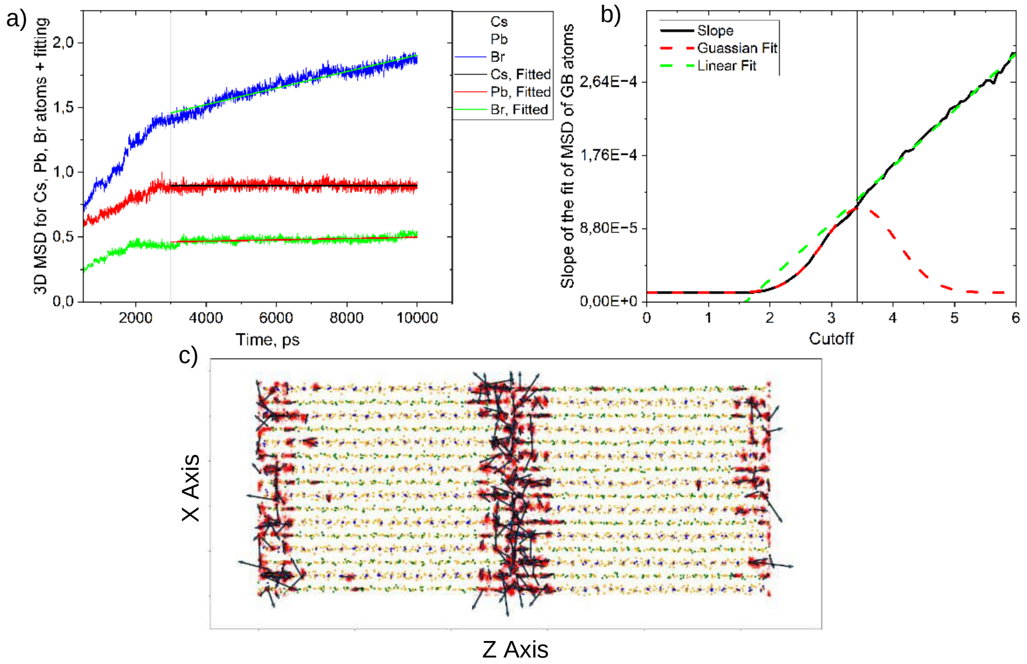

Figure 1. a) 3D Mean squared displacement for every type of atoms in the structure vs. time. b) Slope of the fit of the MSD of grain boundary atoms vs cutoff c) The displacement of GB atoms in the XZ section of the structure.

Time-domain ab initio analysis of facet-dependent carrier dynamics in Cuprous oxide

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Cuprous oxide (Cu_2O) is a promising photoactive material for photoelectrodes used in water splitting and CO_2 reduction.[1,2] A through characterization of charge carrier mobility and recombination dynamics in Cu_2O is important to crucial for understanding its photoelectrochemical (PEC) behavior. Previous experimental study has shown that Cu_2O exhibits varying charge carrier dynamics depending on its crystallographic facet;[3] however, a quantum-level understanding of these variations remains elusive. In this study, we investigate facet-dependent charge carrier dynamics in Cu_2O using real-time quantum dynamics simulations. We performed semiclassical nonadiabatic dynamics simulation with the classical path approximation,[4] and elucidated the quantum mechanisms behind the slower carrier recombination observed at (111) facet, which leads to superior PEC performance.[3]

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Mechanism of lithium dendrite growth on iron surfaces toward high-performance and safe anode-free lithium metal batteries

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Developing higher-energy-density and long-lifetime lithium-based batteries is essential for rapid energy delivery and recharging in emerging electric vehicles and grid energy-storage technologies. Anode-free lithium metal batteries (LMBs) possess an advanced cell configuration with only a bare anode metal foil current collector and no other negative electrode material that can maximize the energy density at the battery-pack level. However, capacity fading and operational safety risks caused by the formation of lithium dendrites impede the practical application of anode-free LMBs. Herein, we evaluated the growth of Li dendrites on an iron substrate surface by performing a series of systematic molecular dynamics simulations based on the embedded-atom method force field to investigate the effects of multiple surface morphologies on the Li atomic deposition and Li dendrite self-healing processes. The kinetics of Li dendrite growth on the atomic scale demonstrate that selecting the Fe(111) surface lattice orientation, reducing undesirable surface cracks, and controlling the surface nanogroove structures can be applied to effectively prevent the formation of irreversible Li dendrites on the surface of the Fe collector, resulting in better battery cell cycling. This work indicates that understanding the mechanism of Li growth on metal surfaces to search for an anode current collector that can significantly improve cell cycling stability is crucial for developing new anode-free LMBs [1].

[1] Liu, S.; Li, N.; Tang, Y.; Mukamel, S.; and Lee, J. Y. "Mechanism of lithium dendrite growth on iron surfaces toward high-performance and safe anode-free lithium metal batteries". *J. Mater. Chem. A,* 12 **(2024)**, pp. 9886-9895. DOI: https://doi.org/10.1039/D3TA07914G

Computational Screening of Multi-Resonance Thermally Activated Delayed Fluorescence (MR-TADF) Molecules for Lasing Application

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Multi-resonance thermally activated delayed fluorescence (MR-TADF) molecules charactering large emission oscillator strengths, effective reverse intersystem crossing (RISC), and narrow emission spectral width, have great potential as laser materials. We propose a molecular descriptor for quick screening MR-TADF molecules as laser candidate materials, $A = \Delta E_{\mathrm{ST}} \sigma_{\mathrm{eff}}^{\mathrm{net,opt}}$, namely, the product of singlet-triplet energy gap and the optical pumping net stimulated emission cross section. Through extensive computations benchmarked with existing experiments, *A* value should be larger than 0.311×10^{-17} cm^2 eV for promising lasing molecules. 119 MR-TADF molecules are virtually designed and only eight molecules are selected as prospective candidates for laser materials through descriptor *A* and spectral overlap.

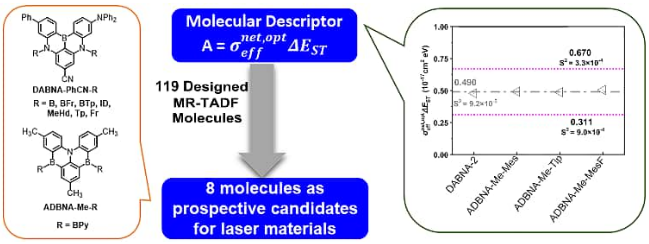

Figure 1. Designed MR-TADF molecules and the value of descriptor *A*.

[1] R. Li, Z. Shuai *Org. Electron.* (2024), 132, 107095.

[2] S. Lin, Q. Ou, Z. Shuai *ACS Materials Lett.* (2022), 4, 487−496.

[3] Q. Ou, Q. Peng, Z. Shuai *Nat. Commun.* (2020), 11, 4485.

Theoretical study on open-shell electronic structures of through-bond/through-space hybrid conjugated systems

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In this study, we theoretically investigated open-shell electronic structures of face-to-face π-stacked *n*-mers of diradicaloid molecules as through-bond/through-space (TB/TS) hybrid conjugation systems. Based on the Hückel theory combined with the valence bond (VB-)based expression of diradical character (y), we defined y for the local TB and TS interactions, y_{TB} and y_{TS}, involved in the π-stacked *n*-mer. We also derived sets of conditions that hold between y_{TB} and y_{TS} when y of the entire *n*-mer system, $y(n)$, takes the maximum for a given n. The relationships between y_{TB}, y_{TS}, and $y(n)$ can help predict and tune the open-shell electronic structures of face-to-face π-stacked *n*-mers of realistic diradicaloid molecules with different y_{TB} [1].

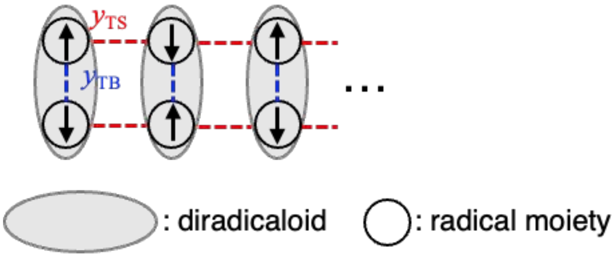

Figure 1. π-Stacked *n*-mers of diradicaloid molecules.

[1] Wataru Yoshida, Hajime Miyamoto, Jinki Shoda, Hiroshi Matsui, Ryota Sugimori, Ryohei Kishi, Yasutaka Kitagawa. "Theoretical study on open-shell electronic structures of through-bond/through-space hybrid conjugated ladder graphs". *Chem. Phys. Lett.* 842 (2024), 141196. DOI: 10.1016/j.cplett.2024.141196.

Computational Study on High-Performance Memristors Utilizing Nanomanipulation and Device Architecture Design

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Memristors as the basic circuit component of neuromorphic chips can be used to realize in-memory computing and parallel data processing. Two prevailing types of memristors, conductive bridge memristors and ferroelectric polarization memristors, were computationally studied to unveil their resistance switching mechanisms and provide possible device design strategies. The kinetic Monte Carlo (KMC) modeling was developed to reproduce filament growth processes in nano-manipulated conductive bridge memristors [1-3]. The computational method was developed to calculate *I*/*R*-*V* curves of two- /multi-terminal ferroelectric polarization memristors and verify their potential synaptic functions [4]. Our computational study provides insights to accelerate the experimental research and development of memristors.

[1] P. Xu, W. Fa, and S. Chen. “Computational Study on Filament Growth Dynamics in Microstructure-Controlled Storage Media of Resistive Switching Memories”. ACS Nano 17 (2023), 10511-10520.

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[3] Y.-C. Li, P. Xu, W. Fa, and S. Chen. Kinetic Monte Carlo Simulations on Electroforming in Nanomanipulated Conductive Bridge Random Access Memories. Nanoscale (2024), DOI: 10.1039/D4NR01546K.

[4] Z. Chen, Y.-C. Li, T.-L. Kong, Y.-Y. Lv, W. Fa, and S. Chen. “Computational Study on Interlocked-Ferroelectricity-Contributed High-Performance Memristors Based on Two-Dimensional Van der Waals Ferroelectric Semiconductors”. ACS Applied Materials & Interfaces 16 (2024): 26428-26438.

Theoretical Studies of 0D-Perovskite Based Luminescent Materials

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A new series of 0D-perovskite structures have been designed and synthesized recently.[1] Due to the large computational cost of TDDFT-PBE0 structural optimization on large periodic systems, we designed an embedded cluster model [2] to handle them.

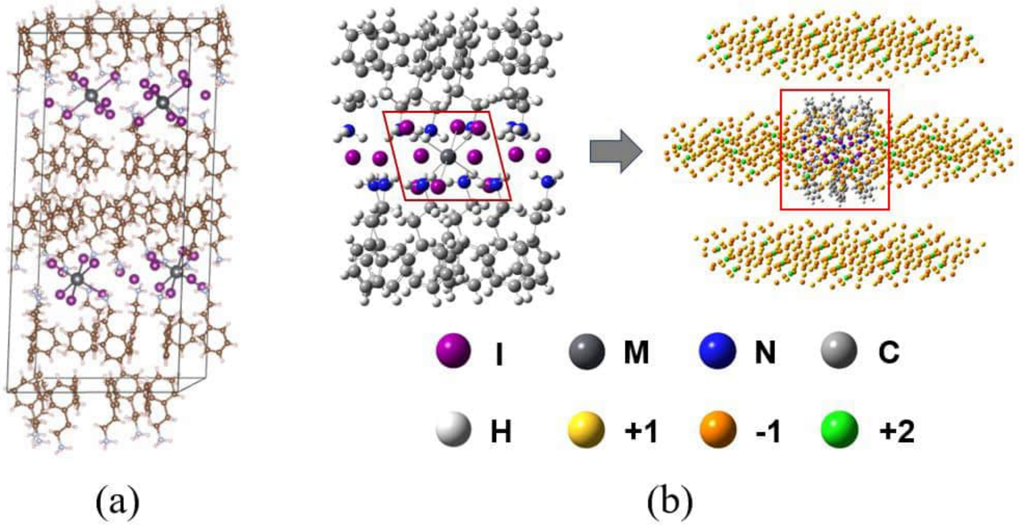

Figure 1. (a) Crystal structures of 0D-perovskite. (b) Diagram of building a cluster model of the 0D-perovskite.

Our model catches two main characters of this series of structures successfully: the various types of interaction between components, and the locality of luminescent process. Our result is in good agreement with experiments and provides reference for luminescent mechanism.

[1] Zheng, N., Cao, S. et al. A General Transformation of 2D to 0D Halide Perovskites by Solvent Incorporation (In preparation).

[2] Sousa, C., Tosoni, S. & Illas, F. Theoretical Approaches to Excited-State-Related Phenomena in Oxide Surfaces. Chemical Reviews 113, 4456–4495 (2013).

Intrinsic Defects in B-Site Columnar-Ordered Halide Double Perovskites $Cs_2AgPdBr_5$

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Since the innovation of the first hybrid organic–inorganic perovskite (HOIPs) solar cell in 2009, its power conversion efficiency (PCE) has rapidly grown from 3.8% to 26.41% within fifteen years. However, practical application of lead-halide perovskites is hindered by the toxicity of Pb and the intrinsic material instability. To overcome these disadvantage, a B-site columnar-ordered halide double perovskites $Cs_2AgPdBr_5$ has been proposed[1]. Considering that its properties may be significantly changed by defects, for example, carrier diffusion limited by deep-level defects, it is important to check the intrinsic defect tolerance of this new material and to find the chemical environment which minimizes the concentration of undesirable defects. We reveal that the influence of Fermi-level pinning can be controlled by adjusting the chemical potential conditions of a halide double perovskite. We find that Ag-poor is a good chemical potential region to grow good p-type $Cs_2AgPdBr_5$. However, deep-level trapping defects may form. Fortunately, partial defects evolve into shallow defect states at 300 K. Only Pd_i and Pd_{Ag} could be the recombination centers. Our study provides a guidance to reduce the intrinsic defects of this class of materials.

[1] G. Ji, C. Han, S. Hu, P. Fu, X. Chen, J. Guo, J. Tang, and Z. Xiao. "B-Site Columnar-Ordered Halide Double Perovskites: Theoretical Design and Experimental Verification". *J. Am. Chem. Soc.* (2021), 143, 10275. DOI:10.1021/jacs.1c03825

Growth kinetics of single-crystal covalent organic frameworks

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Covalent organic frameworks (COFs) have gained attention for their potential in gas separation, energy storage, and catalysis. However, the surprising difficulty of efficiently synthesizing high-quality crystals has long puzzled researchers and limited applications [1,2]. Herein, we employ the GPU-accelerated molecular dynamics simulation software PYGAMD, combined with a dynamic bond model characterized by two key parameters, barrier energy (E_{bar}) and binding energy (E_{bind}), to investigate the growth kinetics of COFs [3,4]. Our analysis indicates that the correlation between E_{bar} and E_{bind} significantly influences the crystallinity of products. Under fast growth conditions (low E_{bar}), the range of E_{bind} suitable for monocrystal formation is very narrow, suggesting that the conditions for reversibility are highly stringent. We also propose a strategy to enhance the defect repair rate by modulating the reaction parameters.

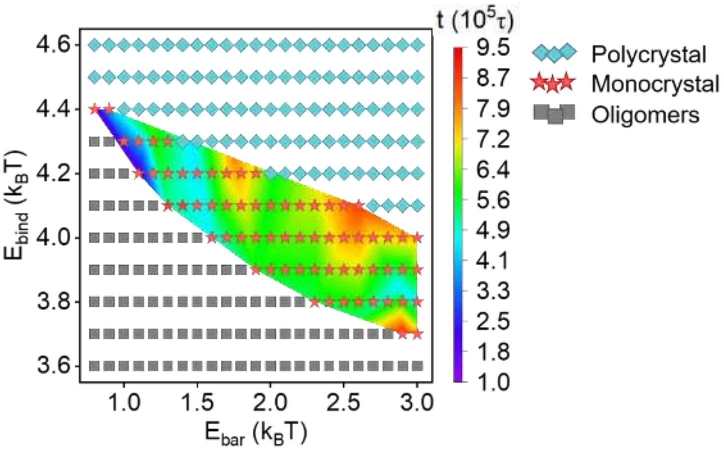

Figure 1. Diagram of COF morphologies as a function of E_{bar} and E_{bind}. The color bar on the right indicates the equilibrium time required for monocrystal formation.

[1] L. Peng, Q.-Y. Guo et al., “Ultra-fast single-crystal polymerization of large-sized covalent organic frameworks”. *Nat. Commun.* 12 (2021), 5077.

[2] J. Han, J. Feng et al., “Fast growth of single-crystal covalent organic frameworks for laboratory x-ray diffraction”. *Science* 383 (2024), 1014.

[3] X.-K. Yu, H.-Y. Zhao et al., “Mechanism for topology selection of isomeric two-dimensional covalent organic frameworks”. *J. Phys. Chem. Lett.* 13 (2022), 7087.

[4] X.-K. Yu, R. Shi et al., “Kinetics of on-surface oligomer formation controlled by concentration”. *Macromolecules* 57 (2024), 5123.

Does the Zimmermann-Traxler transition state always have strong explanatory power? --A combined experimental and computational ‘archaeology of chemistry’ study

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We have developed a synthetic method of CO_2-promoted photo/Ni dual catalyzed allylation of aldehydes with allylic alcohols and revealed the mechanistic insights by mechanistic experiments and quantum chemical calculations. The C=C coordination in the substrate and the LiOAc additive allow the reaction to undergo Ni(0)/Ni(II) oxidative addition with a low energy barrier. The reaction yields a lower stereoselectivity for aryl aldehydes and a higher for alkyl aldehydes, which can be explained by the allylic insertion at the Ni centre in different oxidation states. We find that the lower selectivity in this system corresponds to the model used when the Zimmerman-Traxler transition state was originally proposed. We verify that this missing 1,3-diaxial repulsion is the true origin of the strong explanatory power of the Zimmerman-Traxler transition state.

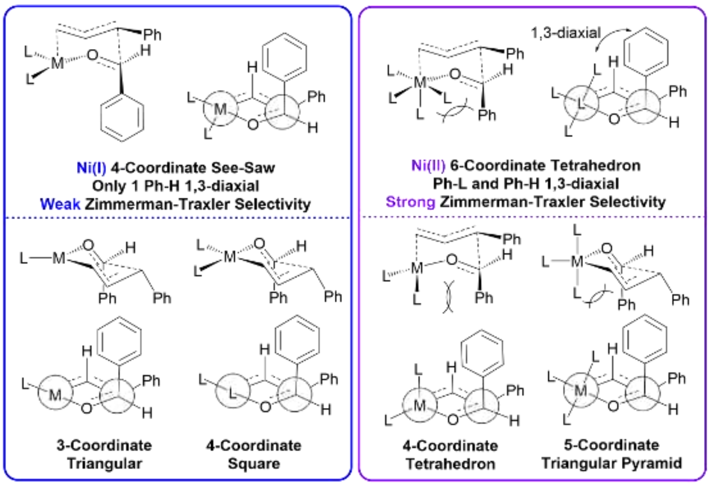

Figure 1. Weak and Strong Explanatory Power of Zimmerman-Traxler TS

[1] Zhang, Zeyu, et al. "Photoredox/Nickel Dual-Catalyzed Allylation of Aldehydes with Allylic Alcohols and Mechanistic Insights in the Presence of CO2." ACS Catalysis 14 (2024): 12392-12402.

Analysis of Organic Reactions by Combinatorial Optimization and Dimension Reduction Method

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I. Introduction

In recent years, an automated reaction path search method has established the concept of a reaction route network [1]. The Reaction Space Projector (ReSPer) visualizes the potential energy hypersurface into a lower-dimensional subspace using principal coordinates [2]. Although ReSPer has been applied to various chemical reactions, it is still challenging to visualize large-scale reaction path networks of organic reactions due to the computational cost. In this study, we implemented the alternative optimization (AO) method, a type of combinatorial optimization, to speed up the ReSPer analysis [3].

II. Results and Discussion

For the validation of the ReSPer-AO method, we randomly generated a dataset of gold clusters and verified the computational time. As a result, it was shown that ReSPer-AO can significantly reduce the computational time compared to the original ReSPer. In this study, we applied ReSPer-AO to the Claisen rearrangement of allyl vinyl ethers to discuss dynamical conformational changes. The details will be reported in the presentation.

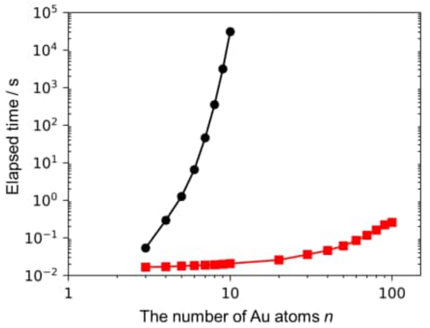

Figure 1. Computational time of ReSPer (black) and ReSPer-AO

[1] S. Maeda, K. Ohno, K. Morokuma, "Systematic exploration of the mechanism of chemical reactions: the global reaction route mapping (GRRM) strategy using the ADDF and AFIR methods". *Phys. Chem. Chem. Phys.*, **2013**, 15, 3683.DOI: 10.1007/s41061-022-00377-7

[2] T. Tsutsumi, Y. Ono, T. Taketsugu, "Reaction Space Projector (ReSPer) for Visualizing Dynamic Reaction Routes Based on Reduced-Dimension Space". *ChemComm (Feature Article)*, **2021**, 57, 11734. DOI: 10.1007/s41061-022-00377-7

[3] L. Qu, T. Tsutsumi, Y. Ono, T. Taketsugu, "Acceleration of Reaction Space Projector Analysis Using Combinatorial Optimization: Application to Organic Chemical Reactions". *submitted.*

Mechanistic Insights into Water Autoionization through Metadynamics Simulation Enhanced by Machine Learning

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People have a long-standing interest in exploring the mechanism of water ionization. The extremely scarce probability of water autoionization in natural conditions obstructs direct experimental probing, and also poses a great challenge to the theoretical community on characterizing the free energy profile and revealing the mechanism. Here, we obtained convergent free energy surfaces through nanosecond timescale metadynamics simulations with classical nuclei enhanced by atomic neural network potentials, which yielded good reproduction of the equilibrium constant ($\mathrm{p}K_\mathrm{w}$=14.14) and ionization rate constant (1.369×10^{-3} s^{-1}). Critical intermediate and transition state were clearly characterized, while an asynchronous mechanism of triple proton transfer was proposed. The solvent-driven effect was described as the dual-presolvation mechanism which contributes to the local electric field fluctuations to trigger the water dissociation. [1]

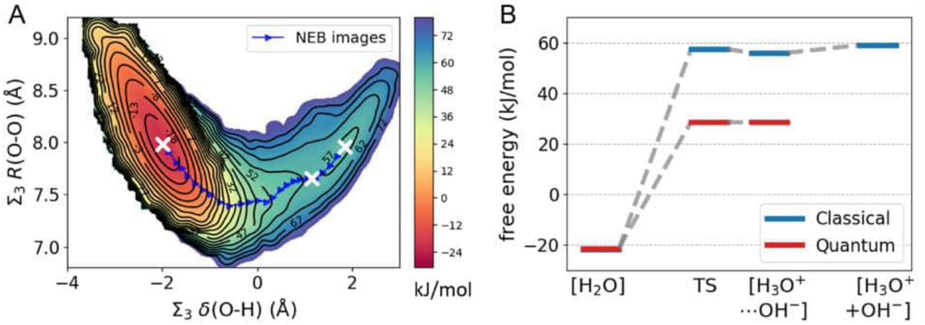

Figure 1. Free energy diagrams for water dissociation calculated with classical and quantum nuclei.

[1] L. Liu, Y. Tian, X. Yang, C. Liu, “Mechanistic insights into water autoionization through metadynamics simulation enhanced by machine learning”. *Physical Review Letters* 131 (2023), 158001.

Enhancing Molecular Data through Quantum Chemical Calculations: An Overview of the PubChemQC Project

RIKEN, Cluster for Pioneering Research

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We initiated the PubChemQC project in 2015 [1-4] and have been continuously developing it ever since. Our goal is to provide a vast amount of quantum chemical data, covering over 80 elements, using mid-range levels of theory such as DFT with a double-zeta basis set. Notably, the PubChemQC JCIM 2017 [2] dataset includes 4 million optimized geometries calculated with B3LYP/6-31G* and 2 million TDDFT/6-31G+* calculations. These datasets can be utilized in machine learning protocols to create models for estimating molecular properties [5]. Moreover, we also released PubChemQC B3LYP/6-31G*//PM6 set, which includes 86 million molecules. In this presentation, we introduce our project and discuss its current status.

Project URL: https://nakatamaho.riken.jp/pubchemqc.riken.jp/

[1] *Maho, Nakata, AIP Conf. Proc.* 1702, 090058 (2015).

[2] Maho Nakata and Tomomi Shimazaki, "PubChemQC Project: a Large-Scale First-Principles Electronic Structure Database for Data-driven Chemistry", J. Chem. Inf. Model., 2017, 57 (6), pp 1300-1308.

[3] PubChemQC PM6: Data Sets of 221 Million Molecules with Optimized Molecular Geometries and Electronic Properties , J. Chem. Inf. Model. 2020

[4] PubChemQC B3LYP/6-31G*//PM6 Data Set: The Electronic Structures of 86 Million Molecules Using B3LYP/6-31G* CalculationsJ. Chem. Inf. Model. 2023, 63, 18, 57345754

[5] **PCQM4Mv2 leader board**
https://ogb.stanford.edu/docs/lsc/leaderboards/#pcqm4mv2

Topic: Machine Learning and Data-driven Approaches

Title: Predicting heat capacity of molecular fluids using interpretable machine learning models: Application of the *Fluid_Thermo* database

Author Name: Simin Li, Yanlei Wang*, and Hongyan He*, Suojiang Zhang

Abstract: Currently, the development of integrated circuits and chips is facing new challenges, with one of the major limiting factors being heat dissipation. Liquid cooling, as one of the most efficient cooling methods, makes the design and synthesis of refrigerant molecules a crucial task. However, the vast variety and diverse structures of liquid media, along with the lack of sufficient thermal property data, present substantial challenges for the design and application of thermal liquid media. In this work, we established the *Fluid_Thermo* database for molecular liquids and ionic liquids (ILs), encompassing 18 different physicochemical and electronic properties, with a total of 18,000 data points. Based on this database, we developed a predictive model for a key property in chemical transport—heat capacity (C_P). Among the models developed, the traditional machine learning algorithm Extreme Gradient Boosting (XGBoost) yielded the best performance, achieving a Pearson correlation coefficient of over 0.99, with an RMSE of 1.95 and an MAE of 0.89, making its heat capacity predictions even more accurate than those derived from DFT calculations. Additionally, we combined DBN and DNN models, successfully applying deep learning algorithms to predictions with small datasets, achieving a Pearson correlation coefficient of 0.96, RMSE of 5.01, and MAE of 2.21.

Scalable and Accurate Chemical Property Predictions Using Universal Neural Network Potentials as Atomic Descriptors

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The universal neural network potential (NNP) is a powerful tool that enables rapid and accurate energy calculations for atomic-level computational simulations, with precision comparable to first-principles methods. In this study, we utilized the valuable latent information of the pre-trained universal NNP to introduce novel atomic descriptors for machine learning. By extracting and utilizing information from the intermediate layers of the NNP, specifically the outputs of the graph neural network (GNN) layer and the multi-layer perceptron (MLP) layer, we constructed predictive models for NMR chemical shifts [1] and molecular adsorption energies on high-entropy alloy nanoparticles [2] (Fig. 1). These descriptors, despite their compactness, achieve accuracy on par with state-of-the-art descriptors, offering a promising approach to accelerate the discovery of new molecules and materials.

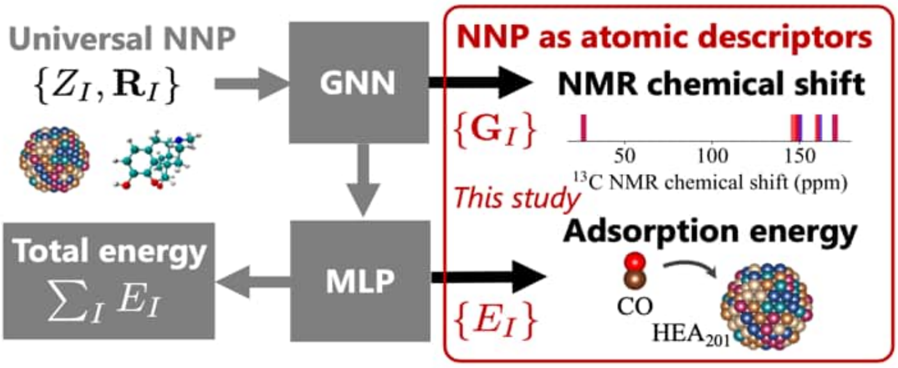

Figure 1. Schematic representation of the universal neural network potential (NNP) model utilizing graph neural networks (GNN) and multi-layer perceptron (MLP) layers to generate atomic descriptors.

[1] T. Shiota, K. Ishihara, and W. Mizukami, “Universal neural network potentials as descriptors: towards scalable chemical property prediction using quantum and classical computers”, *Digital Discovery*, (2024).

[2] T. Shiota, K. Ishihara, and W. Mizukami, “Lowering the Exponential Wall: Accelerating High-Entropy Alloy Catalysts Screening using Local Surface Energy Descriptors from Neural Network Potentials”, arXiv:2404.08413 (2024).

Machine Learning Force Field Construction of Organometallic Complex Materials: An Equilibrium Molecular Dynamics Study on Thermal Conductivity Calculation of Copper Phthalocyanine

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Computing the lattice thermal conductivity of organometallic complex materials has always been an important problem that needs to be solved. Currently, there have been considerable research and work on calculating the lattice thermal conductivity of materials through equilibrium molecular dynamics simulations or non-equilibrium molecular dynamics simulations. However, due to the lack of suitable force fields, the range of materials fields that can be applied to is still very limited. This work uses the active learning method to construct a neural-network based force field, starting from the first-principles data obtained from VASP calculations, and building a neural network force field for dynamic simulations. Currently, reasonable results have been obtained in the copper(II) phthalocyanine system, using the Deep Potential function combined with equilibrium molecular dynamics simulations. The results obtained have better performance than those obtained using the Hybrid-COMPASS force field by previous researchers, and the temperature trends are consistent with experimental results.

An AI-assisted pure density-based nonlocal functional

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van der waals density functional theory(vdw-DFT) is important in many common scenarios, but double integration over grids highly restricts the usage of such functionals. We make use of 3D translation-rotation invariant deep learning neural network and construct a pure density-based nonlocal functional with only single integration over grids. We train our functional by using high level calculation dataset

DES15K[1] of closed-shell molecules and BSE49[2] of open-shell molecules. Our functional can be elaborated to numerical stable high derivatives and thus can support linear response TDDFT and real time TDDFT.

[1] Donchev, A.; Taube, A.; Decolvenaere, E.; Hargus, C.; McGibbon, R.; Law, K.-H.; Gregersen, B.; Li, J.-L.; Palmo, K.; Siva, K.; Bergdorf, M.; Klepeis, J.; Shaw, D. Scientific Data 2021, 8.

[2] Prasad, V.; Khalilian, M.; Otero-de-la Roza, A.; DiLabio, G. Scientific Data 2021, 8.

Fragment-Based Deep Learning for Simultaneous Prediction of Polarizabilities and NMR Shieldings of Macromolecules and Their Aggregates

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Simultaneous prediction of the molecular response properties, such as polarizability and the NMR shielding constant, at a low computational cost is an unresolved issue. We propose to combine a linear-scaling generalized energy-based fragmentation (GEBF) method and deep learning (DL) with both molecular and atomic information-theoretic approach (ITA) quantities as effective descriptors. In GEBF, the total molecular polarizability can be assembled as a linear combination of the corresponding quantities calculated from a set of small embedded subsystems in GEBF. In the new GEBF-DL(ITA) protocol, one can predict subsystem polarizabilities based on the corresponding molecular wave function (thus electron density and ITA quantities) and DL model rather than calculate them from the computationally intensive coupled-perturbed Hartree−Fock or Kohn−Sham equations and finally obtain the total molecular polarizability via a linear

combination equation. As a proof-of-concept application, we predict the molecular polarizabilities of large proteins and protein aggregates. GEBF-DL(ITA) is shown to be as accurate enough as GEBF, with mean absolute percentage error <1%. For the largest protein aggregate (>4000 atoms), GEBF-DL(ITA) gains a speedup ratio of 3 compared with GEBF. It is anticipated that when more advanced electronic structure methods are used, this advantage will be more appealing. Moreover, one can also predict the NMR chemical shieldings of proteins with reasonably good accuracy. Overall, the coste-fficient GEBF-DL(ITA) protocol should be a robust theoretical tool for simultaneously predicting polarizabilities and NMR shieldings of large systems.

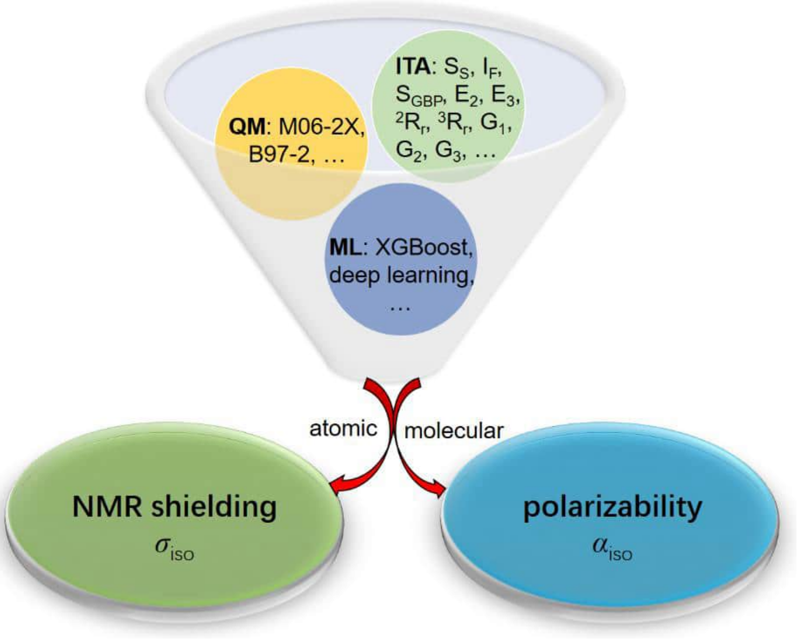

Figure 1. General workflow to predict the response properties (molecular polarizability and the NMR shielding constant). Both molecular and atomic information-theoretic approach (ITA) quantities are used as descriptors for deep learning (DL).

Unveiling the Impact of the Air-Water Interface on Altering Reaction Mechanisms: Incorporating DFT, AIMD, and CMD

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The air-water interface plays a crucial role in numerous chemical and biological processes. In recent years, extensive research has focused on investigating the impact of the air-water interface on reaction properties using advanced computational techniques such as ab initio molecular dynamics (AIMD) [1-2]. This study highlights the significance of considering the air-water interface in understanding and predicting reaction properties in aqueous environments. The results show that the air-water interface can influence the electronic structure and energetics of reactants and intermediates, resulting in modified reaction pathways and thermodynamic properties. The interplay between interfacial water molecules, gas molecules, and reactants at the air-water interface leads to unique hydrogen bonding patterns, solvation effects, and local electric fields, which in turn govern the reactivity and selectivity of chemical reactions. The findings underscore the need for accurate and efficient computational methodologies, such as DFT, AIMD and constrained molecular dynamics (CMD), to capture the dynamic nature of the interface and shed light on the underlying mechanisms that drive the observed enhancements in reaction rates and altered reaction pathways. These insights are crucial for designing and optimizing processes involving reactions at the gas-liquid interface, ranging from atmospheric chemistry to biological systems.

[1] Fang, Ye-Guang, et al. "Mechanistic insight into the competition between interfacial and bulk reactions in microdroplets through N_2O_5 ammonolysis and hydrolysis." *Nature Communications* 15.1 (2024): 2347.

[2] Gong, Ke, et al. "Molecular Mechanism for Converting Carbon Dioxide Surrounding Water Microdroplets Containing 1, 2, 3-Triazole to Formic Acid." *Journal of the American Chemical Society* 146.12 (2024): 8576.

Calculating potential energy surfaces with the variational quantum eigensolver

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The variational quantum eigensolver (VQE) is one of the most commonly used algorithms that does quantum chemistry calculation on near-term quantum computers. Yet VQE isn't able to calculate potential energy surfaces (PESs) efficiently. Since wave functions depend on geometry configurations, the free parameters in the circuit vary with bond lengths, which means parameters must be trained again for a different configuration. In this work, we input bond length values into quantum circuits[1] and introduce mid-circuit measurements[2] so that PESs are calculated with parameter training carried only once. Simulation results show that this method is capable of calculating potential energy curves of small molecules.

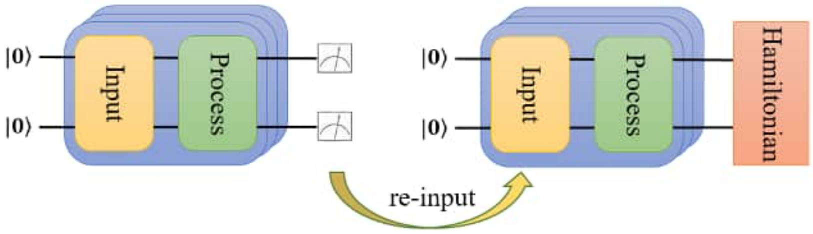

Figure 1. A general structure of circuits proposed in this work. The input units and the processing units alternate with each other. An intermediate measurement is introduced between two parts of the circuit to serve as a nonlinear mapping to the input data.

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Enhancing Variational Quantum Eigensolver with Clifford Transformation and Robust Parameter Optimization

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The variational quantum eigensolver (VQE) framework in quantum computing have opened new avenues for solving complex problems in molecular simulation. Due to the gate error and measurement uncertainty in near term quantum computers, there is a strong need for algorithms optimized for these devices.

In this presentation, we will introduce the Clifford-based Hamiltonian transformation approach, which enhances the accuracy of hardware-efficient ansatz through Clifford transformations. This method allows us to achieve chemical accuracy for systems as large as 12 qubits with fewer than 30 two-qubit gates. Additionally, we will introduce a robust and efficient algorithm that significantly reduces computational overhead for parameter optimization in quantum circuits. Through both numerical simulations and experiments on quantum computers, the algorithm demonstrates faster convergence and greater noise resilience compared to traditional methods. Lastly, we will present the TenCirChem framework, which offers a scalable platform for running quantum circuits with both a tensor network backend and quantum computers. This framework effectively bridges the gap between theoretical quantum chemistry and practical implementation on quantum devices.

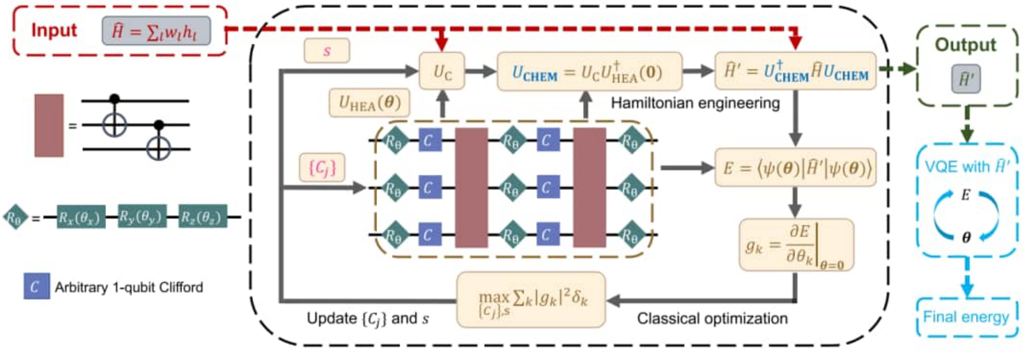

Figure 1. The Clifford-based Hamiltonian Engineering algorithm for variational quantum eigensolver.

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Grid-Based Quantum Simulation of Photoexcited Pyrazine

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We build and examine an end-to-end fault tolerant quantum computing algorithm for simulating absorption spectra and population dynamics of photoexcited pyrazine with a 4D model Hamiltonian. The quantum circuit we construct covers the straightforward initial state preparation, cost-effective time-dependent evolution based on the grid-based Split-Operator Quantum Fourier Transform (SO-QFT) method, and both iterative and canonical phase measurements of vibronic dynamics. We carry out the corresponding cost evaluation using classical emulation and propose a generalised formula for qubit count and gate depth calculation. Our algorithm is also applicable to extended higher dimensional models with no additional gate depth requirements, but only more qubits demanded by adding new vibrational modes as the environmental bath. While quantum devices provide powerful scaling of grid-based space, this approach also benefits a lot from the speed-up efficiency of QFT. This work with its outstanding resource-saving advantages establishes a framework for implementing molecular vibronic studies on real quantum computers.

The application of Hardware heuristic ansatz in periodic system

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The current mainstream superconducting quantum computers have the characteristics of high qubits number but low coherence time, so how to reduce the depth of quantum circuit has a great significance. The most usual Hardware heuristic ansatz is based on Pauli strings excitation operators, which has achieved a great success for calculating ground state energy in small molecule system, we follow this method and using it in a periodic system. Because periodic system has a complex wave function and Hamiltonian, it is a great challenge for variational quantum eigenvalue solver to optimizing the energy, we will solve this problem by expand the operator pool, and using adapt ansatz to reduce the depth of quantum circuit.

Keyword: Hardware heuristic ansatz, periodic system, VQE, Pauli strings

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Uranium Dioxide-Mediated Carbon Dioxide Photoreduction

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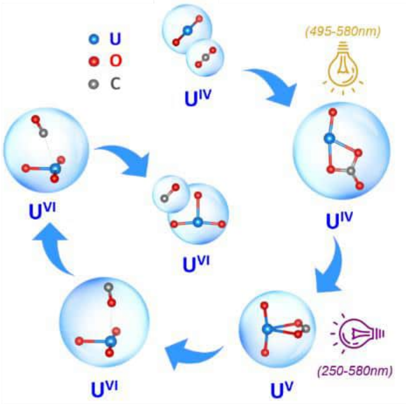
The transition metal-mediated reduction of CO_2 has emerged as an active area with wide interest. Little is known about CO_2 reduction with f-elements. The early actinide elements, in particular uranium, have distinguished performance in multi-electron reduction process because of their facile conversion of oxidation states and bonding ability of 5f/6d orbitals. Herein, CO_2 reduction to CO by tetravalent uranium (U^{IV}) compound UO_2 is investigated via matrix isolation infrared spectroscopy and quantum chemical study. Our results reveal that stable carbonate intermediate $OU^{IV}CO_3$ (**A**) can be prepared at low temperature (4-12 K). Through photolytic reactions of **A** under *visible-light* irradiations (495 nm $< \lambda <$ 580 nm), the charge-separated pentavalent U^V isomer $[U^VO_2]^+[(\eta^2\text{-}O_2C)]^-$ (**B**) is produced due to the electron transfer from U-7s orbital to CO_2 moiety. Sequentially, one C=O bond in CO_2 ultimately breaks by the successive *UV-visible* irradiation (250 nm $< \lambda <$ 580 nm), and the photolysis generates the products CO and hexavalent U^{VI} compound $U^{VI}O_3$ after undergoing two intermediates $U^{VI}O_3(CO)$ (**C**) and $U^{VI}O_3(OC)$ (**D**) with physiosorbed carbonyl group. Moreover, the evolution of oxidation states from electron-rich U^{IV} to U^{VI} on multiple potential energy surfaces of different electronic states involving $U(f^1s^1 \rightarrow f^2 \rightarrow f^1 \rightarrow f^0)$ is further demonstrated.



Scheme 1. Schematic illustration of photoreduction evolution of CO_2 to CO.

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Automated Review Generation Method Based on Large Language Models

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Literature research, vital for scientific advancement, is overwhelmed by the vast ocean of available information. Addressing this, we propose an automated review generation method based on Large Language Models (LLMs) to streamline literature processing and reduce cognitive load. In case study on propane dehydrogenation (PDH) catalysts, our method swiftly generated comprehensive reviews from 343 articles, averaging seconds per article per LLM account. Extended analysis of 1041 articles provided deep insights into catalysts' composition, structure, and performance. Recognizing LLMs' hallucinations, we employed a multi-layered quality control strategy, ensuring our method's reliability and effective hallucination mitigation. Expert verification confirms the accuracy and citation integrity of generated reviews, demonstrating LLM hallucination risks reduced to below 0.5% with over 95% confidence. Released Windows application enables one-click review generation, aiding researchers in tracking advancements and recommending literature. This approach showcases LLMs' role in enhancing scientific research productivity and sets the stage for further exploration.

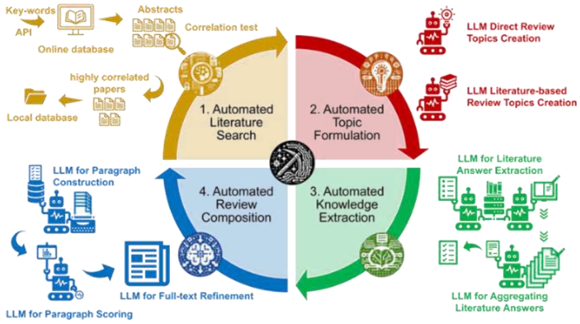

Figure 1. Flowchart of the automated review generation method.

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Coupling Simulations of Spatiotemporal Electromagnetic Fields with Simulations of Ultrafast Photoinduced Dynamics

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Structured light has emerged as an innovative technique that enables the spatial control of laser fields [1]. It could facilitate an optical spectroscopy where the interaction between isolated electric fields (EFs) or magnetic fields (MFs) with matter is investigated selectively. We studied an “MF-only optical spectroscopy” scenario [1], utilizing the finite-differences time-domain (FDTD) method. This study has shown that ultrashort azimuthally polarized beam pulses are excellent candidates for generating isolated MFs (or EFs) at optical frequencies and that metallic nanoantennas can enhance the isolated MFs.

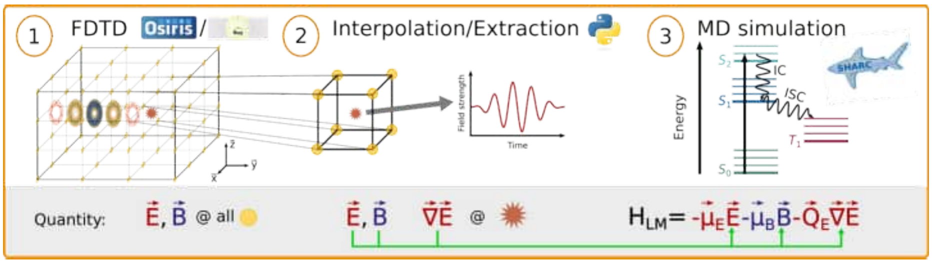

Figure 1. Multiscale protocol coupling FDTD simulations with molecular dynamics simulations.

In this contribution, we will present a multiscale protocol which couples FDTD simulations with nonadiabatic molecular dynamics simulations in the SHARC package [2] to study the dynamics of molecules in presence of arbitrary electromagnetic fields. We will also show applications to the dynamics of lanthanide compounds after excitation of “dark” magnetic dipole-allowed $f \rightarrow f$ transitions.

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Femtosecond Pump-Probe-Spectra in the Heptazine-H_2O Complex: A Computational Study

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Polymeric carbon-nitrides have emerged as promising candidates for sustainable water splitting using solar photons. Its building block heptazine (Hz) has been subjected to various experimental and theoretical studies, investigating its electronic structure and photochemistry when exposed to water.[1-3] While the mechanism has been unraveled[4], the ultra-fast spectroscopic features are still elusive with experimental and theoretical results lacking. In this study we use the Hz-H_2O complex as a model and the isolated Hz monomer as a reference system to simulate its nonadiabatic excited-state molecular dynamics using the state-of-the-art wavefunction method ADC(2). Employing the classical formulation of the doorway-window representation we were able to predict the ground-state bleach (GSB), stimulated emission (SE) and excited state absorption (ESA) contributions to the transient absorption (TA) and two-dimensional (2D) electronic spectra. The results show the features of the ultrafast non-radiative decay of the photoexcited system, with a branching of the wavepacket after about 30 fs. The subsequent population transfer to low-lying excited states is slowed down marginally by the presence of water. The overlap of spectroscopic features for the reactive charge-transfer state in the ESA contribution with the GSB contribution, proofs the importance of theoretical support when investigating TA pump-probe and 2D electronic spectra.

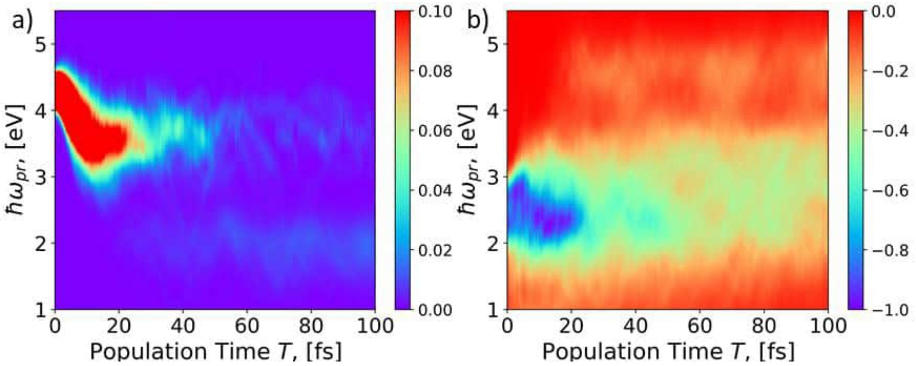

Figure 1: SE (a) and ESA (b) contributions and the total integral signal $S_{int}(T, \omega_{pr})$ as a function of T and ω_{pr} for the Hz-H_2O complex. The pump pulse is tuned to be in resonance with the maximum of the UV-/Vis-absorption spectrum (ω_{pu} = 4.29 eV). The pulse widths are set to $\tau_{pu} = \tau_{pr} = 5$ fs.

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Simulating transient X-ray spectra of molecules and crystals from snapshots along the potential energy surfaces

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The advancement of X-ray free-electron lasers (XFELs) has significantly enhanced cutting-edge experimental research on ultrafast nonlinear X-ray spectra. This progress necessitates the development of corresponding theoretical methods and programs to aid in explaining existing experiments and designing new ones. We have developed ultrafast nonlinear X-ray spectroscopic simulation methods based on non-adiabatic dynamics[1] and snapshots along potential energy surfaces[2]. The latter approach is both economical and practical for large systems. Our predicted fingerprint signals from the dark state in uracil[2] were observed in XFEL experiments involving structurally similar thymine[3], and this method has been further adopted and refined by other researchers[4]. This presentation will focus on our extension of this method from molecules to organic crystals[6] and the copper-dioxygen binding process[7], covering transient X-ray photoelectron & absorption spectra by our in-house code MCNOX [8,9].

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Accurate and efficient NMR shielding calculation with parallel, fully RI-boosted finite 1st derivative framework

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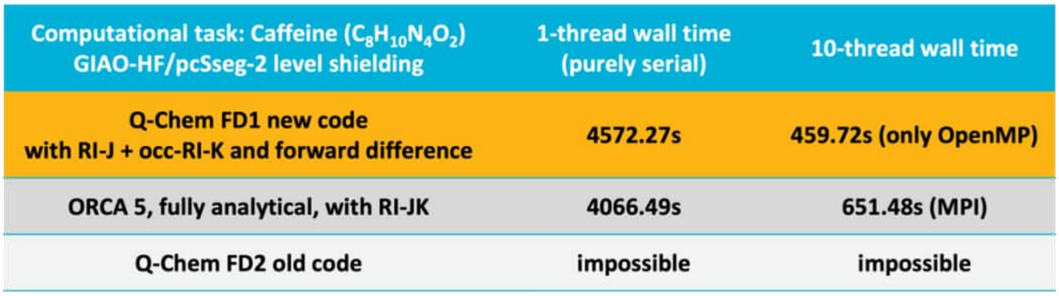
The accurate prediction of nuclear magnetic shielding constants is pivotal for elucidating molecular structure and interactions. Traditional fully numerical methods (finite-difference second derivative) are computationally demanding, while fully analytical approaches require method-specific response equations and often face scalability challenges in the process of solving them. Addressing these limitations, this work introduces a novel implementation that combines finite-difference first-derivative and resolution-of-identity (RI) approximation techniques to achieve accurate and efficient nuclear magnetic shielding at the self-consist field (SCF) level and post-SCF correlated wavefunction method level. This approach facilitates the parallelization of nuclear magnetic shielding computations by applying finite-difference first derivatives with respect to the external magnetic field to the analytical nuclear magnetic moment derivative, which represents the induced magnetic field on each nucleus. The incorporation of resolution-of-identity (RI) based Coulomb (J) and exchange (K) integrals, utilizing conventional RI-JK and occ-RI-K algorithms, further enhances computational efficiency. Preliminary results on Hartree-Fock (HF), density functional theory (DFT) and kappa regularized orbital-optimized Moller-Pollest perturbation theory (k-OOMP2) demonstrate a significant reduction in computational time without compromising the accuracy, thereby offering a promising avenue for molecular NMR calculations where the analytical second derivatives are either unavailable or challenging to derive and implement.



Computational task: Caffeine ($C_8H_{10}N_4O_2$) GIAO-HF/pcSseg-2 level shielding	1-thread wall time (purely serial)	10-thread wall time
Q-Chem FD1 new code with RI-J + occ-RI-K and forward difference	4572.27s	459.72s (only OpenMP)
ORCA 5, fully analytical, with RI-JK	4066.49s	651.48s (MPI)
Q-Chem FD2 old code	impossible	impossible

Figure 1. Parallel timing comparison against old code and ORCA 5.

Linear response pCCD-based methods

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We present the Linear Response pair Coupled Cluster Doubles (LR-pCCD) ansatz and its extension to singles (S), LR-pCCD+S —new mean-field-like computational methods for modeling electronic excitations and transition dipole moments based on pCCD reference function [1] in the PyBEST software package [2,3]. We benchmark these new approaches against the standard EOM-CCSD approach, analyze the effect of orbital optimization within pCCD on the resulting LR-pCCD+S transition dipole moments, and perform a statistical error analysis. We show that the proposed models require only mean-field-like computational cost, while excited-state properties may approach the CCSD level of accuracy [4].

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Individual and cooperative superexchange enhancement in cuprates

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A full understanding of electron correlation in cuprates has been long desired to shed light on the still mysterious high temperature superconductivity. In this study, we address the challenge of achieving high-level ab initio wave function theory calculations, which allow an explicit treatment of dynamic correlations associated with a large number of high-energy orbitals. We elucidate the significant impact of the high-energy virtual orbitals and their cooperative contributions with core orbitals on the superexchange coupling in the lanthanum cuprate, which should have an impact on its emergent superconductivity. A rich collection of mechanisms are revealed, including the orbital breathing effect, the on-site pair excitation effect and the assisted hopping effect. The calculations and physical insights result in reassessment and extension of widely used effective-Hamiltonian models for cuprate-type high-temperature superconductors. This study paves the way for more efficient and accurate ab initio calculations of strongly correlated materials, providing a foundation to establish reliable theoretical descriptions.

This work

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Block-Correlated Coupled Cluster Theory for Accurate Static Correlation of Strongly Correlated Systems

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In order to deal with strongly correlated (SC) systems, our group has proposed the block-correlated coupled cluster (BCCC) method based on the GVB reference (GVB-BCCC in short). The GVB-BCCC*n* (*n*=2,3,4) methods[1-3] with up to *n*-pair correlation have been implemented and can provide accurate results for some strongly correlated systems. Our calculations demonstrate that the GVB-BCCC4 method can provide nearly exact static correlation energies as the density matrix renormalization group method (based on the same GVB orbitals), indicating the importance of four-pair correlation.

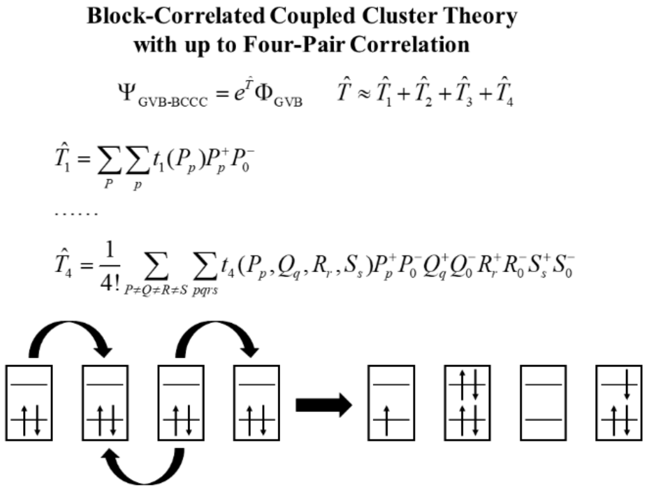

Figure 1. An illustrative picture of four-pair correlation.

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An excitonic model for excited state processes in molecular aggregate

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Excitonic processes in molecular aggregates involve multiple excited state species with different spatial sizes and time scales, as well as complex interactions among them. [1] Meanwhile, these excited state processes are closely related to the efficiency and performance of optoelectronic materials. Therefore, theoretical research on excited state processes is valuable for mechanism investigation, material design, and molecular screening, but it is also highly challenging. Taking advantage of the weak intermolecular interactions in molecular aggregates, we have the construction of a realistic exciton-phonon interaction model based on the localized diabatic states, including the excited state electronic structure containing multi-excited states in the crystal [2] and the fast evaluation of complete exciton-phonon interaction [3]

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When do tripdoublet states fluoresce? A theoretical study of copper(II) porphyrin

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Open-shell molecules rarely fluoresce, due to their typically faster non-radiative relaxation rates compared to closed-shell ones. Even rarer is the fluorescence from states that have two more unpaired electrons than the open-shell ground state, since they involve excitations from closed-shell orbitals to vacant-shell orbitals, which are typically higher in energy compared to excitations from or out of open-shell orbitals. States that are dominated by the former type of excitations are known as tripdoublet states when they can be described as a triplet excitation antiferromagnetically coupled to a doublet state, and their description by unrestricted single-reference methods (e.g., U-TDDFT) is notoriously inaccurate due to large spin contamination. In this work, we applied our spin-adapted TDDFT method, X-TDDFT, and the efficient and accurate static-dynamic-static second order perturbation theory (SDSPT2), to the study of the excited states as well as their relaxation pathways of copper(II) porphyrin; previous experimental works suggested that the photoluminescence of some substituted copper(II) porphyrins originate from a tripdoublet state, formed by a triplet ligand $\pi \rightarrow \pi^*$ excitation antiferromagnetically coupled with the unpaired d electron. Our results demonstrated favorable agreement between the X-TDDFT, SDSPT2 and experimental excitation energies, and revealed noticeable improvements of X-TDDFT compared to U-TDDFT, not only for vertical excitation energies but also for adiabatic energy differences. These suggest that X-TDDFT is a reliable tool for the study of tripdoublet state fluorescence. Intriguingly, we showed that the aforementioned tripdoublet state is only slightly above the lowest doublet excited state and lies only slightly higher than the lowest quartet state, which suggests that the tripdoublet of copper(II) porphyrin is long-lived enough to fluoresce due to a lack of efficient non-radiative relaxation pathways; an explanation for this unusual state ordering is given. Indeed, thermal vibration correlation function (TVCF)-based calculations of internal conversion, intersystem crossing, and radiative transition rates confirm that copper(II) porphyrin emits thermally activated delayed fluorescence (TADF) and a small amount of phosphorescence at low temperature (83 K), in accordance with experiment. The present contribution is concluded by a few possible approaches of designing new molecules that fluoresce from tripdoublet states.

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QUEST#4X: an extension of QUEST#4 for benchmarking multireference wavefunction methods

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Given a number of datasets for evaluating the performance of single reference methods for the low-lying excited states of closed-shell molecules, a comprehensive dataset for assessing the performance of multireference methods for the low-lying excited states of open-shell systems is still lacking. For this reason, we propose an extension (QUEST#4X) of the radial subset of QUEST#4 [1] to cover 110 doublet and 39 quartet excited states. Near-exact results obtained by iCIPT2 (iterative configuration interaction with selection and second-order perturbation correction) are taken as benchmark to calibrate SDSCI (static-dynamic-static configuration interaction) and SDSPT2 (static-dynamic-static second-order perturbation theory), which are minimal MRCI and CI-like perturbation theory, respectively. It is found that SDSCI is very close in accuracy to ic-MRCISD (internally contracted multireference configuration interaction with singles and doubles), although its computational cost is just that of one iteration of the latter. Unlike most variants of MRPT2, SDSPT2 treats single and multiple states in the same way, and performs similarly as MS-NEVPT2 (multi-state n-electron valence second-order perturbation theory). These findings put the SDS family of methods (SDSPT2[2,3], SDSCI[2], and iCIPT2[4], etc.) on a firm basis.

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Triple electron attachments with a new Intermediate-Hamiltonian Fock-space coupled-cluster method

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The Fock-space coupled-cluster(FSCC) theory is a multireference coupled-cluster theory for excitation energies(EEs), ionization potentials(IPs), electron affinities (EAs), double ionization potentials(DIPs), and double electron affinities(DEAs). The intermediate Hamiltonian FSCC(IHFSCC) methods have been developed to handle intruder states and convergence problem. Calculating triple electron-attached(TEA) states with FSCC has also been proposed recently.[1] However, computing TEAs requires $S^{(2,0)}$ no matter whether the IHFSCC method is employed or not, which entails calculating all DEA states in the active orbital space. If the number of active orbitals is large, it will be expensive and intruder states may also arise. Recently, Meissner proposed an IHFSCC scheme that only requires $S^{(1,0)}$ to calculate TEAs.[2] This allows for the use of larger active spaces in calculating TEAs. This new IHFSCC method is actually an extension of the STEOM-CC method for TEAs. We implemented the new IHFSCC method for TEAs and calculated triple ionization energies and excitation energies of atoms with a p^3 configuration and molecules with $\sigma^1\pi^2$ configuration. Previous research indicates that the accuracy of FSCCSD results is closely related to the size of the active space, where more reasonable results are obtained with a greater number of active orbitals.[3] However, our findings suggest that for calculating triple ionization energies of these systems, using the minimum active space yields more reasonable results compared with those using a larger active space. In addition, the number of active orbitals has a negligible effect on their excitation energies. Furthermore, the orbitals employed in IHFSCC calculations can influence results on TEAs and more reasonable results are achieved using target-state orbitals than those using reference-state orbitals.

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Exhaustive Screening of Topological High-fold Degenerate Semimetal with Chiral Structure

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After topological insulators (TIs) have aroused widespread concern about the nontrivial properties of materials, this topological classification has been extended from insulator to metal, resulting the discovery of many different kinds of topological semimetals (TSMs). Other than traditional Dirac and Weyl fermions, exotic massless fermionic excitations with nonzero Berry flux could also exist in TSMs. Such TSMs, which has been called high-fold degenerate semi-metals, always has a larger topological charge and a longer Fermi arc. It is reported that the existence of such exotic fermions is protected by crystal symmetry [1] and non-magnetic chiral crystals with spin-orbit coupling could have these topological electronic properties [2]. Most of the current TSMs are found in achiral structures, where two Weyl fermions with opposite chirality are restricted to the same energy by symmetry. However, there is no such limitation in chiral structures, which makes chiral TSMs found to have special properties such as quantized circular photogalvanic effect, gyrotropic magnetic effect and more. For further research, high-throughput calculation and screening are carried out by classification of space groups (SGs) from the perspective of crystal symmetry. Among the 65 chiral SGs that we calculated, a total of 147 materials from 15 SGs which host these fermions near the Fermi energy have been found. Because the degeneracy of the high-fold degenerate fermions is related to irreducible representation dimensions of high symmetry points, we can clearly observe the law of the distribution of these high-fold degenerate fermions in SGs. Within these TSMs, not only four-fold fermions and six-fold fermions have been found in high symmetry points, but also Weyl fermions are distributed in the Brillouin region. Multiple Fermi arcs that span the surface Brillouin zone can be observed. Our results confirm the existence of unconventional chiral fermions and conventional Weyl fermions in high-fold degenerate semi-metals, which makes it a promising platform for exploring the physical properties of chiral fermions.

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Magnetic topological Weyl fermions in half-metallic In_2CoSe_4

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Magnetic Weyl semimetals (WSM) [1] have recently attracted much attention due to their potential in realizing strong anomalous Hall effects. Yet, how to design such systems remains unclear. Based on first-principles calculations, we show here that the ferromagnetic half-metallic compound In_2CoSe_4 has several pairs of Weyl points and is hence a good candidate for magnetic WSM. These Weyl points would approach the Fermi level gradually as the Hubbard U increases, and finally disappear after a critical value U_c. The range of the Hubbard U that can realize the magnetic WSM state can be expanded by pressure, manifesting the practical utility of the present prediction. Moreover, by generating two surface terminations at Co or In atom after cleaving the compound at the Co-Se bonds, the nontrivial Fermi arcs connecting one pair of Weyl points with opposite chirality are discovered in surface states. Furthermore, it is possible to observe the nontrivial surface state experimentally, e.g., angle-resolved photoemission spectroscopy (ARPES) measurements. As such, the present findings imply strongly a new magnetic WSM which may host a large anomalous Hall conductivity [2].

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The description of Atom and Bond Reactivity in the Language of Conceptual Density (Matrix) Functional Theory

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In the context of the growing impact of conceptual density functional theory (CDFT) as one of the most successful chemical reactivity theories, response functions up to second order have now been widely applied; in recent years, among others, particular attention has been focused on the analytic evaluation of these response functions and extensions to higher order have been put forward.[1] The traditional CDFT gives sharp definitions for a set of well-known but vaguely defined concepts such as chemical potential (electronegativity) and hardness/softness. In addition, it gives access to regioselectivity, electro-/nucleophilicity through local reactivity descriptors such as the Fukui function and (hyper)polarizability via a nonlocal (non)linear response function.[2-3] In our study, their performances are compared between the analytical approach with the wildly used finite difference approximation. In the same spirit of traditional CDFT, we further extended its matrix formalism called conceptual density matrix functional theory (CDMFT) for the description of the reactivity or property of chemical bonds in molecular systems. With the quantity defined in CDMFT, i.e., Fukui matrix, we illustrate that the derivative of bond order with respect to the number of electrons is closely related to the difference of force constant and bond distance between natural and ionized systems.[4]

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Structure and Dynamics at Pt/Water Interfaces Revealed by Machine Learning Molecular Dynamics

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The altered solvation structures and dynamics of interfacial water molecules directly influence the elementary steps of electrochemical reactions. Simulations of interfacial structure and dynamics provide a crucial molecular-level foundation for interpreting experimental observables. To address the inherent accuracy-efficiency trade-off and gain dynamical insights, we employ state-of-the-art machine learning molecular dynamics (MLMD) to investigate water adlayer dynamics, which govern interfacial water reorganization at metal/water interfaces. This work demonstrates how spatial correlations in desorption events accelerate water exchange dynamics at Pt(111) and Pt(100)/water interfaces [1]. This mechanism extends to stepped Pt/water interfaces. To illustrate this, we first show how water pairing within the adlayer induces anisotropic water dynamics (diffusion, hydrogen bonding, and reorientation) at Pt(211)/water interfaces [2]. This analysis is then extended to Pt(S)-[n(111)×(100)] surfaces (n = 2, 3, 4, 7, 9), demonstrating the utility of water ring density as an order parameter for characterizing water exchange dynamics at these interfaces [3].

Keywords: Machine learning molecular dynamics，Pt/water interfaces，water exchange dynamics

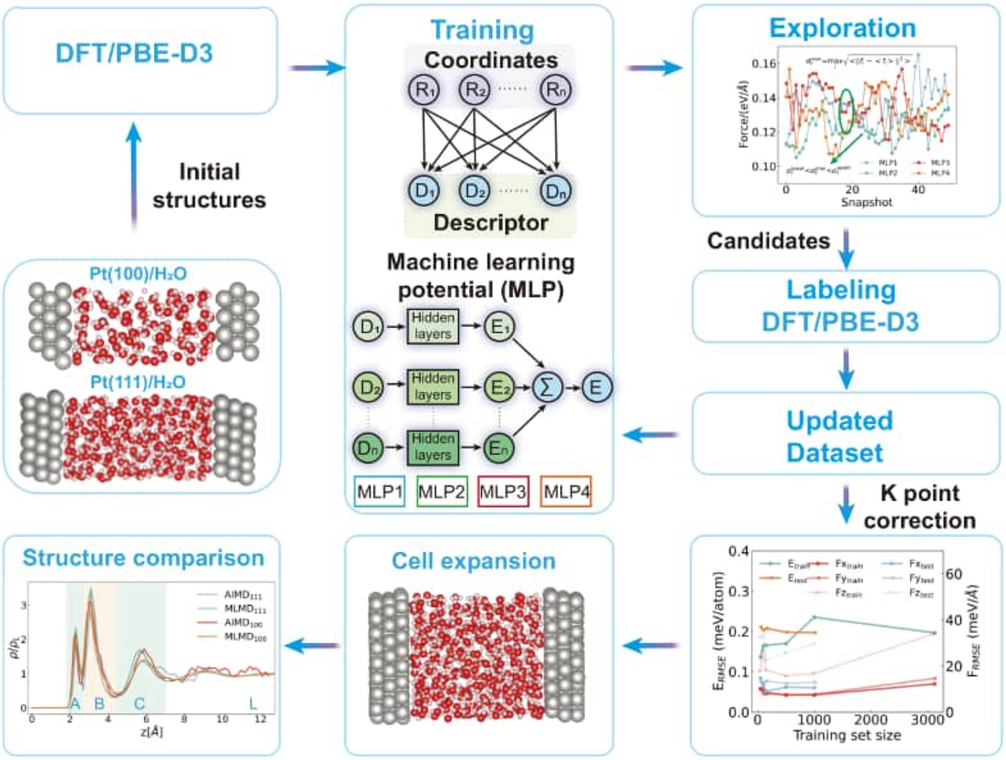

Figure 1: Schematic illustration of the construction, validation, and application of the machine learning potential(MLP) for Pt/water interfaces.

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Dimensionality Reduction in Electronic Structure Theory via Nonlinear Dynamics and Machine Learning: Classical and Quantum Computing Aspects

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The holy-grail of electronic structure theory in both classical and quantum computing domains is solving Schrodinger's equation accurately with minimal resource requirements. While classical electronic structure methods such as coupled cluster (CC) theory requires a higher-order polynomial scaling, its unitary variant suited for quantum computing architecture suffers from deep quantum circuits and huge number of measurements. To address such problems, we propose a framework leveraging concepts from nonlinear dynamics that exploits the nonlinear optimization trajectory for dimensionality reduction in both classical and quantum computing paradigm. Our method suggests an adiabatically decoupled structure in the many-body operator space consisting of a *principal* and an *auxiliary* sub-part. Such a decoupling projects the effective optimization problem into an extremely lower dimensional principal manifold that drastically reduces the quantum and classical resource utilization. Further, we establish a mathematical formalism such that the higher dimensional *auxiliary* ones are predicted from the lower dimensional *principal* subspace only either via machine learning[2] or analytical algebraic expressions[1]. The subsequent resource-efficient inclusion of the *predicted* operators ultimately ensures the desired accuracy without incurring any computational overhead. The methods show extremely accurate results and the advantages are particularly conspicuous under realistic hardware noise of quantum computers[1].

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Multivalent Interactions in Sequence Mediated Spontaneous Association of short RNA Chains

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Quantifying bimolecular self-assembly is pivotal for understanding cellular function. Association of protein, DNA and RNA components in cell and formation of biomolecular condensate are found important factors for controlling different biological processes. In this context the major focus of current research is elucidating how the biomolecular sequence and cellular environment are connected to condensate formation and properties. RNA-RNA association and phase separation appear to essential for the assembly of stress granules, underlie RNA foci formation in repeat expansion disorders. RNA molecules are found to play significant role in gene-regulatory functions via condensate formation among themselves, or with RNA binding proteins. The interplay between driven versus spontaneous processes are likely to be an important factor for controlling the formation of RNA mediated functional biomolecular condensate. However, the sequence specific interactions and molecular mechanisms that drive the spontaneous RNA-RNA association, and help to form RNA mediated phase separated condensate remain unclear. With microseconds long atomistic molecular simulations we studied how essential aspects of RNA chains, namely base composition, metal ion binding and hydration properties, contribute to association of the series of simplest biologically relevant homopolymeric and heteropolymeric short RNA chains. We show that spontaneous processes make the key contributions governed by the sequence-intrinsic properties of RNA chains, where the definite roles of base specific hydrogen bonding and stacking interactions are prominent in association of the RNA chains. Ionic association and nucleobase specific interactions of Na^+, K^+ and Mg^{2+} ions with RNA chains show the impact of ionic environment in RNA-RNA association. We identified several long-lived cation-N/O and water-N/O pairs within the associated RNA chains. Our results also imply that purine versus pyrimidine contents of RNA chain can directly influence association properties of RNA chains by modulating hydrogen bonding and base stacking interactions. Overall, our findings are expected to provide molecular basis and atomistic insight about sequence mediated association properties of RNAs that can leads phase separation, and facilitate RNA granules and foci formation in cell.

Quantitative Studies of the Key Aspects in Selective Acetylene Hydrogenation on Pd(111) by Microkinetic Modeling with Coverage Effects and Molecular Dynamics

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Selective acetylene hydrogenation as a vital industrial reaction has been studied for decades. However, some key issues remain elusive. Herein, a detailed microkinetic model using DFT energies is developed to comprehensively investigate the key aspects of acetylene hydrogenation on Pd(111). The coverage-dependent kinetic simulation, factoring in both self and cross-interactions of adsorbates as well as the coverage effects on the transition states of each elementary step, is compared with the coverage-independent kinetic calculation derived from energies obtained at low coverages. The accurate determination of the free energy barrier of ethylene desorption using *ab initio* molecular dynamics (AIMD) with umbrella sampling adds further crucial insights into the microkinetic model. By combing the coverage-dependent calculations and AIMD results, we achieve a full first-principles kinetic simulation with all the kinetic parameters being systematically calculated to understand the acetylene hydrogenation. We show that the coverage-dependent microkinetic model gives a much more reasonable TOF result of 1.41 s^{-1} at 300 K than that calculated using coverage-independent model (3.16×10^{-24} s^{-1}). The microkinetic results, including activity and selectivity, are tested against experimental data, yielding a good agreement.

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Multiscale Regulation of Light-Harvesting and Quenching in LHCII protein

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Major light-harvesting complex of photosystem II (LHCII) is a photoreceptor protein that regulates energy transfer and dissipation in response to rapid fluctuations of light intensity, directly affecting the efficiency of photosynthesis. In this presentation, I will describe the collaborative and interdisciplinary investigations combining multiscale computational chemistry calculation, time-resolved IR/Raman spectroscopy and Cryo-EM structure determination to understand the mechanism of energy transfer and dissipation in LHCII. We found that the ultrafast distortion of intermediate Sx state of lutein significantly enhances their electronic coupling with chlorophylls in LHCII by 30% to 50%, substantially promoting the overall excitation energy transfer. At longer timescale, both elevated temperature and acidification triggers an allosteric regulation of the global protein conformational changes induced by local conformational transitions. The dynamic motions induce close contacts between the associated chromophores to facilitate fluorescence quenching and excess energy dissipation. These findings highlight LHCII as an exquisite quantum switch regulating photosynthesis.

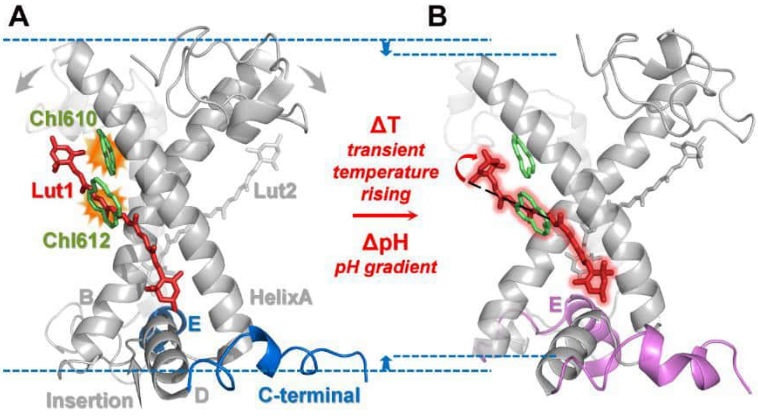

Figure 1. Allosteric regulation of photoprotection in LHCII.

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Long-range electron tunneling through protein junctions

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Motivated by the rapid development of nanobioelectronics, we performed multiscale computer simulations based on classical molecular dynamics (MD), electronic-state calculations within density functional theory (DFT), and electronic coupling calculations to investigate coherent tunneling transport in protein junctions. Factors determining charge transport mechanisms (coherent tunneling vs. incoherent electron hopping) and their distance dependencies will be discussed together with the effects of the adsorption structures, solvation, and temperature on the junction.

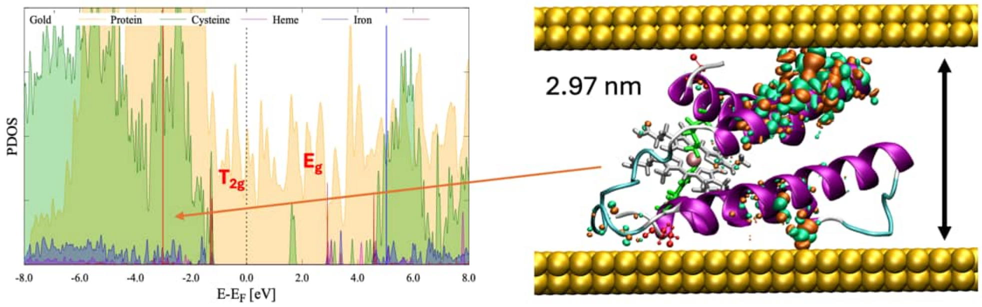

Figure 1. Electronic states (left) of Cyt b_{562} gold junction (right) with one of the dominant conduction channels (green/orange lobes).

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Accelerating Reliable Multiscale Quantum Refinement of Protein–Drug Systems Enabled by Machine Learning

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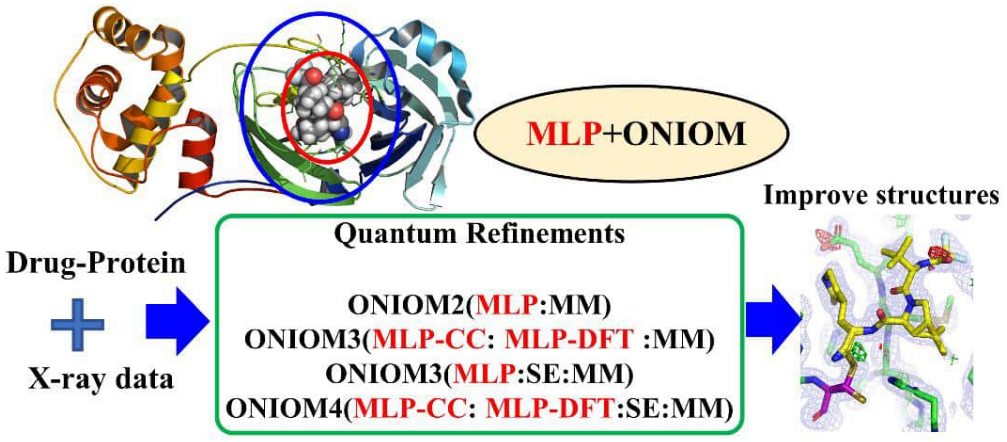
Accurate atomic structures of biomacromolecules are crucial for drug development and biocatalysis. X-ray diffraction (XRD) is a common method for determining these structures. Traditionally, X-ray crystallographic refinement combines molecular mechanics (MM) force fields with experimental XRD data. However, quantum refinement, pioneered by Ryde and colleagues, replaces MM with more accurate quantum mechanics (QM) methods to describe protein key sites and improve local structures.[1] We propose combining multi-scale ONIOM with QR methods (**ONIOM_QR**) and incorporating robust machine learning potentials (MLPs) to enhance refinement efficiency and reliability.[2-3] By applying this unique MLPs+ONIOM-based QR method, we successfully refined 50 protein–drug/inhibitor systems, achieving reliable results even for challenging systems with charged groups.



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ReaxFF Force Field Parameter Optimization Based on Enhanced Sampling Algorithm

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ABSTRACT: Understanding the interaction between water and metal surfaces is crucial for fields such as corrosion protection, catalysis, and microelectronics. Increasing attention is being drawn to the dynamic evolution of metal surfaces driven by their interactions with water molecules. Reactive force field (ReaxFF) combined with molecular dynamics (MD) served as an essential tool for investigating the reaction dynamics of complex systems. However, conventional ReaxFF parameter optimization techniques, such as sequential single-parameter parabolic extrapolation, strongly depend on initial guesses based on training experience, which limits their wider applications. To overcome the limitations, we developed an enhanced sampling method that uniformly generates parameter combinations across the high-dimensional space and iteratively refines the search around promising regions. This approach significantly improves the efficiency and accuracy of finding the initial guess. Incorporating this enhanced sampling (ES) algorithm, we evaluated three optimization methods, such as machine learning optimization (MLopt), refined enhanced sampling optimization, and conventional optimization. After a comprehensive evaluation total error, parameter variation, and energy prediction accuracy, the ReaxFF force fields optimized by SE-MLopt method were selected for investigating the oxidation behavior of Cu in water.

Stability of Ru@Sn_9 *Zintl* cluster on a CeO_2 (111) surface and its catalytic activity in Water-Gas-Shift (WGS) reaction.

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Cerium Oxide (CeO_2) is one of the most efficient compounds and supporting surface because of the facile changes in oxidation state between Ce^{4+} to Ce^{3+} and is widely used in high-performance oxygen storage applications and catalytic redox reactions, solid oxide fuel cells, water-gas shift reactions, etc. The use of *Zintl* clusters or metalloids rather than isolated noble metal atoms as a catalytic center offers the potential to exploit the interactions between transition and main-group metal to achieve low-barrier reactions, and some recent works suggest that *Zintl* clusters are effective catalysts for some important reactions (e.g. WGS, r-WGS, methanation etc.). Recently, Sun et al. have reported the selective reduction of CO_2 over highly dispersed $RuSnO_x$ sites, derived from a $[Ru@Sn_9]^{6-}$ Zintl cluster but an atomic-level understanding of mechanism, and how it relates to the electronic properties of the cluster remain unclear. [1]

In this work, we firstly investigate the stability of the Ru@Sn_9 Zintl cluster on the CeO_2(111) surface by comparing the optimized energy of the cluster on the surface with a dispersed structure where the Ru and Sn atoms are dispersed on the surface, using periodic Density Functional Theory (DFT). Interestingly, in many cases clusters prove not to be stable on surface, but rather are disrupted by strong metal-support interactions (SMSI). [2] An important first objective therefore is to establish the stability of the Ru@Sn_9 cluster on the surface under normal reaction conditions. It has been found that Ru@Sn_9 cluster will disperse over the surface and accumulate in a monolayer where Ru would prefer to stay at the edge. Later, we report some studies on the $RuSn_9/CeO_2$ (111) catalyst for WGS reaction where the possible reaction mechanisms have been explored and activation energy barriers have been calculated. This catalyst shows a significantly lower energy barrier using different reaction paths, compared to other reported heterogeneous catalysts such as Au, Pt, Cu nanoparticles on supported surfaces.

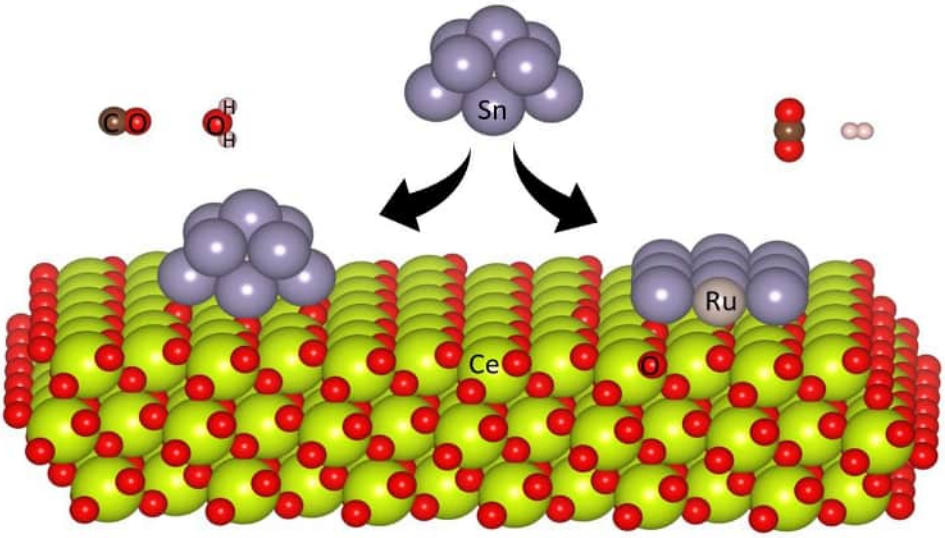

Figure 1. Landing of Ru@Sn_9 cluster on the surface and Water-Gas-Shift Rection.

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Theoretical Investigation of Fe-based Perovskite for Chemical Looping Partial Oxidation of Methane

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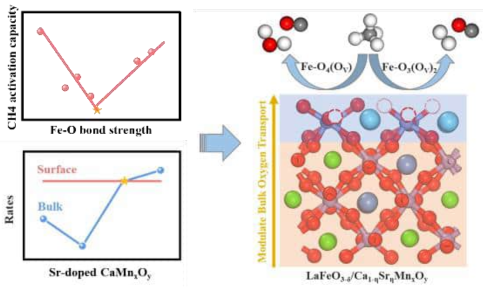
Chemical looping partial oxidation of methane (CL-POM) is a promising technology for syngas production. However, the dynamic changes in surface and bulk structures of the oxygen carrier (OC) during the oxidation-reduction reactions complicate the understanding of key factors influencing activity and selectivity [1-3]. To address this, we employed DFT calculations to investigate the continuous reaction process of methane on $LaFeO_{3-\delta}$ surfaces, analyzing the relationship between surface structure and reaction performance. Then we introduced a second OC to supply oxygen to the surface. We found that the Fe-O bond strength of $LaFeO_{3-\delta}$ exhibits a volcano relationship with methane activation capability, related to the band gap states of d bands of Fe and the downward shift of the O p-band center. The coordination number descriptor CN_d effectively describes Fe-O bond strength, also following a volcano relationship. We further proposed constructing $LaFeO_{3-\delta}/Ca_{1-\eta}Sr_{\eta}MnO_3$ interfaces, with Sr^{2+} doping in $CaMnO_3$ to modulate oxygen diffusion. Our findings suggest that 25% Sr^{2+} doped $CaMnO_3$ achieves a balance between surface reaction and bulk oxygen diffusion, and Sr^{2+} doping can suppress the phase transition of $CaMnO_3$. This study provides insights into CL-POM and suggests a potential composite oxygen carrier material.



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Importance of Material Surface Structure for Photocatalytic Reactions in Water

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Photocatalysis has been a promising method for water decontamination, particularly for persistent organic pollutants. The efficacy of photocatalysis depends on photocatalysts and their photoelectric properties. Substantial efforts have been made to promote pollutants degradation by tuning the electronic structures of photocatalysts. However, such approaches often result in increased costs and limited enhancements. Recent studies indicate that the surface structure of photocatalysts, including exposed facets, can significantly affect performance.[2] To elucidate the underlying mechanisms, this work uses first-principles calculations to investigate PFOA degradation processes on TiO_2 and In_2O_3 surfaces (Fig. 1). The results indicate that the interfacial water and surface atomic coordination are critical factors. These insights could provide valuable guidance for the design of more effective photocatalysts.

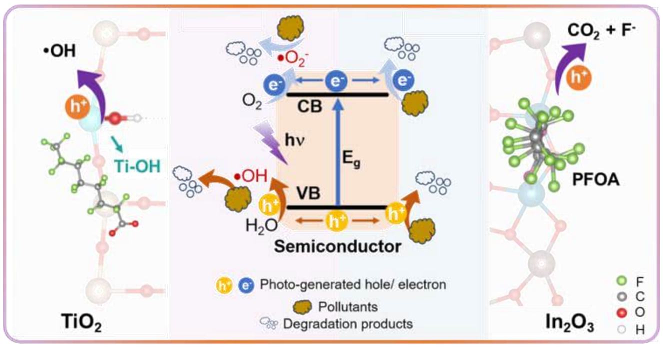

Figure 1. Schematic diagram of pollutants degradation process on the surface of photocatalysts.

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Computational insights into how Co/Mn dopants stabilize RuO_2 catalyst under OER conditions

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Water electrolysis powered by renewable energy sources is a pivotal strategy for achieving carbon neutrality through the production of green hydrogen. However, the efficiency of this process is hindered by the sluggish anodic oxygen evolution reaction (OER), which contributes significantly to the overall overpotential. Despite their effectiveness in minimizing this overpotential, RuO_2 catalysts are prone to rapid dissolution under acidic OER conditions. In this study, we use density functional theory (DFT) calculations to provide atomic-level insights into the dissolution mechanisms of RuO_2 and evaluate the impact of Co and Mn dopants on enhancing catalyst stability. Utilizing a kink RuO2 model that can predict experimental overpotential data[1], we investigate the structural and electrochemical properties of the catalyst under operational conditions. We establish the dissolution process at the active kink site, which is considered the source of dissolution, with four proton-coupled electron transfer steps. Introduction of Co and Mn dopants was found to modify the electronic environment at the kink site. Cobalt doping reduced the OER overpotential by 14%, while manganese doping did not alter the already low overpotential. Both dopants increased the dissolution overpotential, suggesting their role in stabilizing the catalyst by preserving the active sites. Crystal orbital Hamilton population (COHP) analysis indicated that the introduction of these dopants strengthens the bond between kink Ru and the anchoring oxygen, providing a mechanistic explanation for the stabilization. These results highlight the potential of doping strategies in developing more durable and efficient catalysts for water electrolysis.

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Theory-driven catalyst design for propane dehydrogenation

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Propylene is an important chemical raw material. Propane dehydrogenation is a promising route for propylene production, in which the preparation of efficient catalysts is the key [1]. However, the microenvironment of catalytic sites is complex and changeable, theory-driven catalyst design is thus desirable. In this paper, the design criteria of catalysts are studied. For alloys, a research strategy of "direct prediction of catalytic performance by the catalytic microenvironment" is proposed, developing a "degree-of-isolation" descriptor to predict the selectivity of propylene [2,3], and an "exponential function" descriptor for evaluating the activation ability [4]. For oxides, a highly active and stable catalyst is developed by regulating the strong metal-support interaction at the interface [5].

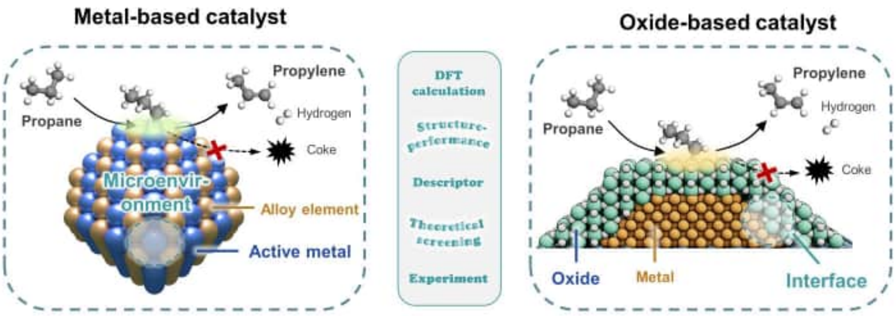

Figure 1. Theory-driven catalyst design for propane dehydrogenation.

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Properties of Metal-Supported ZnO Films and Their Application in Water Splitting

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ZnO overlayers covering metal supports find applications in sensors, catalysis, microelectronics, and optical devices. Density functional (DFT) calculations were applied to characterize properties of periodic ZnO monolayers supported on close-packed surfaces of various metals (Ru, Pd, Pt, Cu, Ag, Au, Sn, and Pb) under hydrogenation conditions. Thermodynamic analysis revealed high stability of the films on most metals, except insufficiently reactive Sn and Pb. Metal-oxide interactions are found to have a significant and locally uneven effect on the electronic structure of ZnO. Compared to pristine ZnO, the supported ZnO films show a higher propensity for H adsorption and O vacancy formation. As a result, under hydrogenation conditions supported ZnO films are calculated to adsorb significant quantities of H or develop O vacancies, unlike pristine ZnO. Using ZnO/Ag as a representative system for the water-splitting reaction, it was found that the overpotentials of HER and OER were about 0.10 V and 0.76 V, indicating ZnO films with metal support could be effective catalysts for water splitting. The calculations reveal how the metal support affects the composition, stability and reactivity of ZnO films, offering valuable insights for the rational design of ZnO-metal interfaces in catalytic applications.

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Kinetic Simulations of Methanol Steam Reforming and CO_2 Hydrogenation

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Kinetic simulation of surface reactions is essential for comprehensive understanding of a chemical process. Currently there are two predominant microkinetic models: mean-field microkinetic model (MF-MKM) and kinetic Monte Carlo (kMC) method. Though highly efficient, predictions from MF-MKM may be inaccurate because of neglecting the spatial correlations. Contrarily, kMC simulations can yield more accurate results. However, kMC method often encounters stiff problems originated from the significant rate difference. We proposed a scheme (ads-kMC) to solve the stiff problems due to the fast diffusion and adsorption and desorption processes and applied the scheme to analyze the mechanism of methanol steam reforming over PdZn(111) and CO_2 hydrogenation to ethanol on $Pd_2Cu(110)$. The results demonstrate that ads-kMC overcomes the over-smoothing problem in log-kMC algorithm well and predicts similar results as MF-MKM when the diffusion is very fast and adsorbate interactions are neglected. The simulated selectivity from ads-kMC and MF-MKM is close to each other and agrees with the experimental values well for both systems. Investigations on CO_2 hydrogenation indicate that diffusion rates affect the simulated selectivity of ethanol noticeably, indicating that it is important to consider and treat diffusion correctly in kinetic simulations.

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How to Achieve Both Stability and Activity in Fe-N-C Electrocatalysts for ORR: Unifying Roles of O and S Doping

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The development of oxygen reduction reaction (ORR) catalysts is crucial in energy and materials science. The Fe-N-C family, known for its cost-effectiveness and high activity, is a promising alternative to platinum-group metals, yet maintaining stability remains challenging. This study explores the electrochemical stability of pyridinic and pyrrolic FeN4 structures using an implicit solvent model under constant potential. We found that pyrrolic FeN_4 is easy to protonated in acidic environments, leading to Fe dissolution and catalyst deactivation. In contrast, FeN_4 demonstrates increased stability in alkaline environments due to axial coordination. Doping with O and S in acidic conditions decreases protonation of pyrrolic N, enhancing stability, while in alkaline environments, it boosts the activity of both pyridinic and pyrrolic FeN_4. Mechanistic analysis reveals that O and S weaken electron-withdrawing effect of N, reducing density of state of p orbital and increasing valence electrons of Fe, thereby enhanceing the stability and activity. This study provides theoretical insights into improving the durability and activity of Fe-N-C catalysts.

Efficient and Flexible Approach for Local Distortion: Distortion Distribution Analysis enabled by Fragmentation

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Various theories have been developed to understand chemical processes. Among these theories, distortion/interaction model is one of the most popular ones.[1] For interaction energy analysis, many theories/models were developed to further decompose interaction energy into detailed terms. On the other hand, few methods were also merged to successfully analyze distortion into local part for certain systems like mechanochemical systems and macromolecules.[2-3]

Herein, we propose an efficient and flexible approach for analyzing local distortion enabled by fragmentation framework. In our approach, two strategies are utilized to estimate and visualize molecule's distortion distribution after fragmentation. Our approach was used to successfully help locate the most distorted regions of several different chemical and biological systems. Moreover, our approach can be applied to multiple structures and several computational codes/methods.

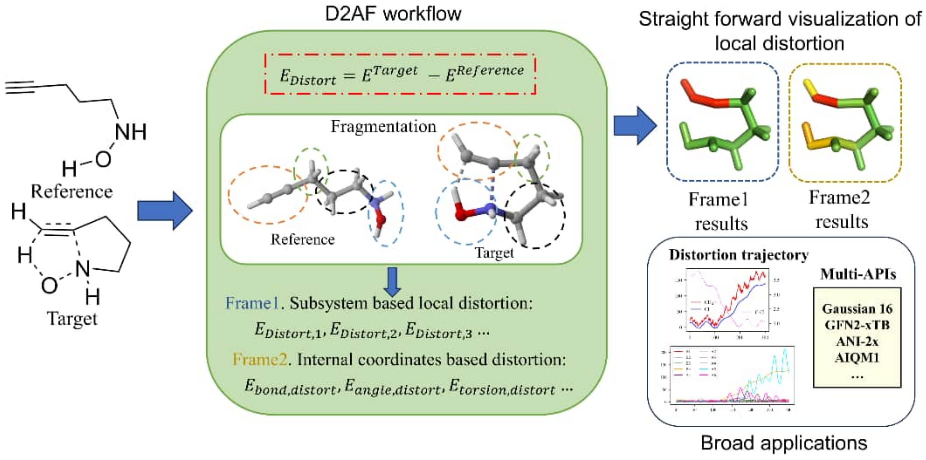

Figure 1. Workflow of D2AF

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The Role of Bases and Silver(I) Additives in the Ligand-Promoted β-C(sp^3)-H Heteroarylation of Free Carboxylic Acids

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Carboxyl group is one of the most basic and extensive functional groups in organic chemistry. It is of great significance to realize carboxylic acid-oriented C-H activation in this field. Recently, Yu *e*t al. reported the first catalytic example of Pd^{II}-catalyzed mono-selective β- and γ-C(sp^3)-H aza-heteroarylation of free carboxylic acids[1]. Herein, we investigated the above reaction mechanism and revealed the roles of bases and silver additives. The calculated results showed that the reaction involves the β-C(sp^3)-H activation and the C-C coupling processes. This work provides a new understanding of the molecular mechanism of carboxylic acid-oriented C(sp^3)-H bond activation[2].

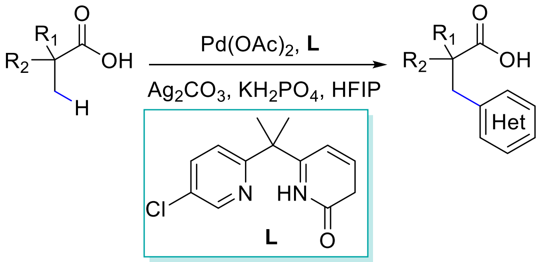

Figure 1. β-C(sp^3)-H heteroarylation of carboxylic acids.

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Noncollinear functional construction schemes in different dimensions

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Due to the lack of noncollinear spin density functional form, the traditional spin collinear functional in Density Functional Theory (DFT) may not deal with the system with noncollinear spin direction. However, by utilizing the multicollinear approach, the noncollinear functional with the independent variable of 3d space vector field can be constructed from traditional collinear functional.

In this paper, we derive the analytical form of the noncollinear functional when the independent variable is a 2d space vector field and give the concrete form of the noncoplanar functional of the 3d space vector field derived from the coplanar functional of the 2d space vector field. Furthermore, we prove that the functional form derived from 1d to 3d to 2d is consistent with the functional directly derived from 1d to 2d, and the functional derived from 1d to 2d to 3d is consistent with the functional directly derived from 1d to 3d, which illustrates the rationality of the multicollinear approach. This approach provides a continuation method for functionals satisfying rotation invariance, which may have applications in the construction of energy functionals.

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From collinear functionals to noncollinear functionals

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Recently, we have presented a scheme, called multicollinear approach [1], for generalizing collinear functionals to noncollinear ones. Different from the local projections of spin magnetization vectors used by Kübler *et al.*, our approach adopts global projections, thus guaranteeing the collinear limit condition and maintaining numerical stability.

This scheme has been implemented in PySCF to handle issues such as generalized Kohn-Sham, non-collinear TDDFT, and spin-flip TDDFT [2]. Here, I focus on some of the latest developments, including:

1. real-time TDDFT;
2. spin-flip TDDFT gradients;
3. the development of noncollinear nonlocal functional;
4. more general mathematical formulations in other dimensions.

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Exact constraint of density functional approximations at the semiclassical limit

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We explore the ħ→0 limit of density functional theory, which is known as the semiclassical limit. By introducing an effective ħ to generic real-world many-electron systems, we show that the strongly correlated systems, which have been a challenge for mean field density functional theory, are in some sense semiclassical. We derive the asymptotic constraints for the exact density functional in the semiclassical limit, which is violated by all the commonly used conventional density functional approximations. Such constraints may be essential for systematically improving the performance of density functional approximations on strongly correlated system. The semiclassical perspective also suggests a new picture of chemical bonds that is different from the molecular orbital theory, where the overbinding tendency of local density approximation can be analytically explained. As a side remark, we find that some extremely challenging systems for multi-configuration method are actually very simple with a semiclassical representation. Such contrasts suggest that one can develop a quantum chemistry framework that is different from the one-electron picture, which would be naturally more proper to deal with strongly correlated systems.

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A pointwise machine learning correction to eliminate error cancellation in density functional approximation

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Recently, the integration of machine learning (ML) with density functional theory (DFT) has emerged as a potent strategy to enhance the capabilities of DFT. Our work endeavors to develop a machine learning model that maps several local descriptors onto energy density corrections for the B3LYP, utilizing high-precision total energies of atoms and molecules as reference data in training. To test the generality of our ML-corrected DFAs, we also conducted further tests in more benchmark sets. As results, our ML-corrected DFAs, with comparable or even superior computational efficiency compared with its parent functional, improves various thermochemical and kinetic energies, such as atomization energies, ionization potentials, electron affinities, bond dissociation energies, and barrier heights. This suggests that our approach has the potential to perform better than mainstream DFAs in practical applications.

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Snap-shots of cluster growth: electronic structures of a Zintl ion with a linear Fe_3 core, $[Fe_3Sn_{18}]^{4-}$

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Endohedral Zintl clusters are a type of intermetallic compound in which transition metal atoms are encapsulated in a cage composed of *p*-block elements. A high-spin iron-tin binary anion – $[Fe_3Sn_{18}]^{4-}$ with a linear Fe_3 core was synthesized and investigated by DFT.[1] For the Fe-Fe bonds, an unoccupied σ* orbital and a pair of degenerated singly occupied π* orbitals are observed. Regarding their doubly occupied bonding counterparts, each Fe-Fe bond can be described as 1/2σ+1/2π. The structure of the Sn_{18} cage can be considered as an intermediate state between the separated and fused ends. The Walsh diagram in Figure 1 shows that two antibonding orbitals locating on two groups of Sn-Sn bonds between Sn_9 fragments, are lifted above the Fermi level respectively in the stepwise coalescence process of Sn_{18}.

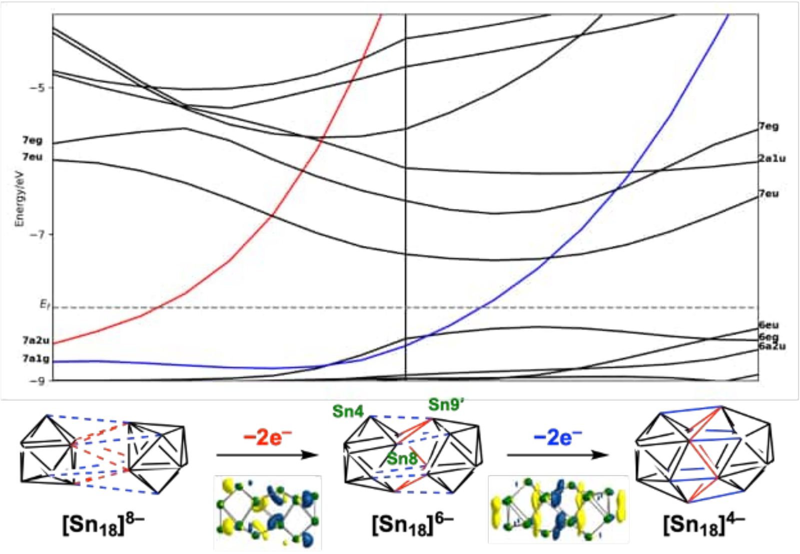

Figure 1. The Walsh diagram showing the coalescence of the two Sn_9 polyhedra to a single ellipsoidal Sn_{18} unit.

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Exact Factorization-Based Density Functional Theory Beyond the Born-Oppenheimer Approximation: Case Study of a Model System

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In this work, we conduct calculations on a 1D two-electron Shin-Metiu model, showing that nonadiabatic effects of proton coupled electron transfer (PCET) process can be precisely captured using a density functional approach based on exact factorization (EF) [1]. There is an abrupt change of electronic density at position of the avoided crossing in the adiabatic potential energy surface. And this avoided crossing would invalidate Born-Oppenheimer approximation. Compared to the exact result, the critical position shifts by about 1.2 Bohr. A rigorously derived correction, added to the exchange-correlation potential in density functional theory, captures this effect very accurately. In our previous work [2], we investigated this phenomenon using EF based density functional theory (DFT) on a two-site Hubbard model and proposed a local conditional density approximation (LCDA) of the correction term. Here, we exceed the grid model and propose a concrete functional form of LCDA which could be applied in real systems. The correction of orbital energy is also discussed implying potential application of this method in band structure renormalization in electron-phonon systems.

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Dynamic Correlation in Single-Ion Magnets Using Density Matrix Embedding Theory

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Magnetic anisotropy of single-molecule magnets can be attributed to splitting of energy levels due to spin-orbit coupling between ground state and excited states. For transition metal and lanthanide ions, the energy of 3d or 4f orbitals split under crystal fields, and such localized near-degenerate orbitals cause ground state and excited states to have multi-configurational character. Spin-orbit coupling based on complete active space and further multireference perturbation give accurate zero-field splitting parameters (referred to as CAS-SISO), but its expensive computation cost limits the calculation to even simple systems. Based on locality of strong correlation interactions, quantum embedding method allow us to perform high-level calculation on impurity based on low-level method solution on whole system. Density matrix embedding theory (DMET) is quantum embedding method based on density matrix, and show excellent performance in combination with CASSCF and SISO. In this work, we test the robustness of DMET+NEVPT2 on different coordination environments calculations to see the effect of DMET on dynamic correlations. DMET and all-electron calculation agree very well. And since we restrict orbitals participated in perturbation calculation also in the impurity, the computation cost of NEVPT2 is greatly reduced, due to high scaling of PT2 calculation. The results suggest that for magnetic anisotropy of single-molecule magnets, DMET can describe static and dynamic correlations efficiently, which make further spin-relaxation calculation viable.

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Dynamical Mean-Field Theory of the Holstein Polaron: Solving the Impurity Green's Function by Discretizing the Hybridization Function

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The dynamical mean-field theory (DMFT) has been widely studied in strongly correlated electron systems by mapping lattice models onto quantum impurity models subject to a self-consistency condition. As a dual problem of electron-electron correlation, DMFT has also been proved to show excellent performance in treating electron-phonon correlation. The Holstein polaron has been studied by DMFT where the impurity Green's function is solved by continued fraction expansion [1, 2]. We attempt to solve the Anderson-Holstein impurity problem by discretizing the hybridization function to obtain the impurity Hamiltonian to solve the Green's function. Such a framework provides a general solution to DMFT-based electron-phonon correlated problems and offers new routes to deal with electron-phonon correlation.

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Towards realistic simulation of material with correlated method

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Performing *ab-initio* simulations on real materials presents a dual challenge for quantum solvers in terms of achievable accuracy and computable size. Systematically Improvable Quantum Embedding (SIE)[1] using correlated methods as high-level solver holds promise in addressing this challenge, owing to its ability to capture the correlation dominating material nature and the intrinsic fragmentation feature of its algorithm. This study improves the SIE to achieve state-of-the-art level accuracy and developed a corresponding high-performance GPU-accelerated software package, attempting to verify the algorithm's capability on various real-world systems. SIE was applied to a highly delocalized water+graphene system encompassing nearly 400 atoms, aligning the results under both open and periodic boundary conditions to confirm its capacity to simulate real material properties. Consequently, the authors further discovered a unique finite size error cancellation mechanism existing within this system which may bring new insight in this scenario.

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Dual-Mode Floquet Quantum Master Equation for Electronic Transport in a Bichromatic-Driven Quantum Dot

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Exploring quantum systems through simultaneous drivings with two frequencies is a forefront area in physics and chemistry. The validity of multi-mode Floquet theory in analyzing closed quantum systems beyond periodic perturbations has recently been demonstrated. In this study, we expanded our previously developed Floquet quantum master equations (FQME) for open quantum systems [1] for scenarios with two time-periodic drivings. Our dual-mode FQME (DM-FQME), rooted in two-mode Floquet time evolution within the Hilbert space. We applied the method to investigate quantum transport through a two-level dot with weak system-lead coupling subjected to two drivings. Notably, our findings suggest that the conductance of two-level dots exhibits finer steps when frequencies are non-identical. Furthermore, our analysis reveals differences in quantized conductance between systems driven by two frequencies compared to a single frequency. The DM-FQME approach holds promise for facilitating molecular dynamics studies (Floquet surface hopping methods) under a bichromatic radiation field.

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Machine Learning Assisted First-principles Simulation of Tunneling Phenomena in Spectroscopy

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Spectroscopy is an important experimental technique for probing molecular structure, properties, and reaction kinetics. The tunneling phenomena of atoms (including heavy atoms) and molecules can be measured through spectroscopic experiments, primarily manifested as isotope effects in reaction rates and level splitting in ro-vibrational spectra (also known as tunneling splitting). Therefore, first-principles simulations of tunneling in reaction kinetics and tunneling splitting in molecules are of great significance for elucidating the physical and chemical processes behind experimental phenomena. Ring-polymer instanton theory is a method for calculating tunneling rates and tunneling splitting using the minimum action tunneling pathway [1,2]. It can be combined with first-principles methods to understand tunneling phenomena in larger molecules. Here, I will report on some progress we have made in tunneling simulations in recent years by combining instanton theory, high-level electronic structure calculations, and machine learning-assisted tunneling path optimization algorithms [3]. For example, we have theoretically reproduced the significant $^{16}O/^{18}O$ isotope effect observed in matrix-isolation spectroscopy experiments, providing strong theoretical support for oxygen atom tunneling [4]. We have also simulated the "fingerprints" (i.e. tunneling splitting) left by the tunneling of heavy atoms and whole molecules in molecular rotational spectra.

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Memory Kernel Coupling Theory: Obtain Time Correlation Function from Higher-order Moments

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Dynamical observables can often be described by time correlation functions (TCFs). However, efficiently calculating TCFs for complex quantum systems is a significant challenge, which generally requires solving the full dynamics of the systems. This Letter presents the memory kernel coupling theory (MKCT), a general formalism for evaluating TCFs. The MKCT builds upon Mori's memory kernel formalism for TCFs. Our theory further decomposes the memory kernel into auxiliary kernels. Rapid decay of auxiliary kernels allows us to truncate the coupled equations of motion with high accuracy. Notably, only higher-order moments are sufficient as the input for obtaining TCFs. While this formalism is general, we carry out the numerical demonstration for a typical open quantum system–the spin-boson model.

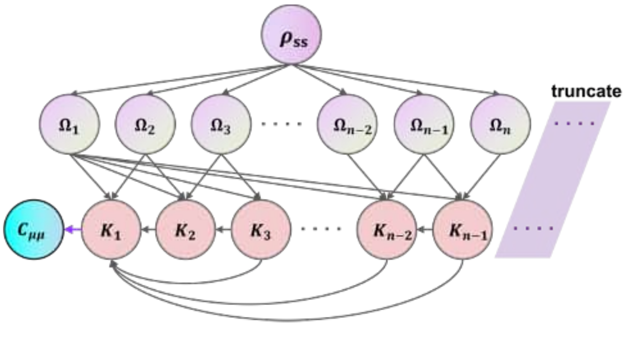

Figure 1. A schematic diagram of MKCT.

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New Insights into Phase Space Representations for Finite-State Quantum Systems and Applications in Nonadiabatic Transition Dynamics

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Because of the substantial energy gap between potential surfaces of different electronic states, electronic degrees of freedom in chemical systems are typically treated as finite-state quantum systems. The study of dynamics of finite-state quantum systems is instrumental in better understanding nonadiabatic transitions.

For two-state quantum systems, we propose a novel class of phase space representations for exact population dynamics utilizing positive semi-definite non-covariant phase space functions, time-dependent weight functions on constraint phase space, and time-dependent normalization factors. The triangle window function approach proposed in Reference 1 leads to its special case. For general finite-state quantum systems, we introduce novel phase space representations incorporating triangle window functions for exact electronic dynamics involving electronic coherence terms. When these representations are combined with the recently developed nonadiabatic field (NaF) dynamics, we achieve satisfying computational results in various models of nonadiabatic chemical systems.

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The exact solution to the finite size one dimension model

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INTRODUCTION

As opposed to straightfoward computation of internal energy in computer simulations, evaluation of thermodynamic properties related to free energies is challenging and demands much more computing resources. It then becomes very useful to understand the finite-size effect theoretically such that accurate results could be possibly extrapolated from simulations of a rather smaller system for the purpose of reducing computational cost. In this poster, we focus on the finite-size effect on the chemical potential μ(N) evaluated by the widely used particle insertion method of Widom.

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Theoretical Analysis of X-ray Spectra of Water *

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INTRODUCTION

The elastic X-ray scattering amplitude is the square of the modulus of the Fourier transform of the electron density:

$$I(\mathbf{k}) = \left| \int_{-\infty}^{\infty} \rho_e(\mathbf{r}) e^{i\mathbf{kr}} d\mathbf{k} \right|^2$$

It reflects the overall distribution of electrons in a substance, also known as form factor. When people want to analyze the distribution of local electrons in a substance, such as the electron cloud morphology of a single molecule in bulk water, the independent atom hypothesis was born, that is, using the form factor of a single atom to approximate the overall form factor of the substance, which is the application of the electron distribution of a single atom to approximate the overall electron distribution of the substance in real space.

In the past, people usually used the form factor of a single atom in an independent free state, and ignored the influence of bonding and the environment on the distribution of the atomic electron cloud, although some people later proposed a deformation form factor. However, based on our discussion, the new form factor meets two principles. First, the new form factor must be the form factor of the atom in an independent free state. Second, the electron distribution of the single atom corresponding to the new form factor in real space must conform to physical reality, such as the electron density distribution must be non-negative.

JOB DESCRIPTION

We proposed a new form factor, and then compared the X-ray elastic scattering amplitude of a single water molecule in the gas phase and bulk water calculated by DFT, showing that when all form factors are optimized, our form factor can significantly reduce the error, and the corresponding physical properties of water in real space, such as dipole moment and quadrupole moment, are equivalent to the exact results, while other existing form factors have some inconsistencies in real space, such as the dipole moment of water molecules in the IAM form factor is 0, and the electron density of the MAFF form factor is negative, etc.

Secondly, a method is proposed to correctly calculate the elastic X-ray scattering amplitude after using the pseudopotential basis set in aiMD, and a self-consistent method for optimizing parameters is proposed for MAFF and our form factor.

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Stability of Quantum Systems beyond Canonical Typicality

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Involvement of the environment is indispensable for establishing the statistical distribution of system. We analyze the statistical distribution of a quantum system coupled strongly with a heat bath [1]. This distribution is determined by tracing over the bath's degrees of freedom for the equilibrium system-plus-bath composite. The stability of system distribution is largely affected by the system-bath interaction strength. We propose that the quantum system exhibits a stable distribution only when its system response function in the frequency domain satisfies $\tilde{\chi}$ $(\omega=0+)>0$. We show our results by investigating the non-interacting bosonic impurity system from both the thermodynamic and dynamic perspectives [2]. Our study refines the theoretical framework of canonical statistics, offering insights into thermodynamic phenomena in small-scale systems.

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Mechanisms of the interlayer charge transfer in two-dimensional heterostructures: nonadiabatic molecular dynamics investigations

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Abstract: Two-dimensional semiconductors and heterostructures advance novel optoelectronic devices, where the interlayer charge transfer plays a crucial role. Employing the nonadiabatic molecular dynamics (NAMD) approach, the short- and long-range interlayer charge transfer in TMD heterostructures are systematically investigated. In the first work [1], we focus on the spin-orbital coupling (SOC) effect in organic/inorganic hybrid heterostructures, revealing that the SOC effect not only fascinates the interlayer electron transfer, but also fascinate the spin flip process by promoting couplings between two spin channels. In the other work [2], the effect of hexagonal boron nitride (hBN) intercalation on the long-range charge transfer in $MoSe_2/WSe_2$ systems is investigated thoroughly. The interlayer hole transfer process from $MoSe_2$ to WSe_2 is retarded by 2-3 orders of magnitude upon the hBN intercalation, while the interlayer hole transfer would exist even after three-layer (3L) hBN intercalation. Utilizing the linear electron-phonon coupling model, the role of the hBN intercalation in the interlayer hole transfer is uncovered. On the one hand, the increased layer distance induced by the hBN intercalation would suppress the direct ultrafast hole transfer channel completely. On the other hand, a novel channel intermediated by unoccupied orbitals of WSe_2 becomes dominant, where the intralayer shear mode of hBN contributes to reducing the energy barrier of such a channel to achieve a remarkable quantum tunneling process. This work thoroughly explores the unique effect of hBN layers on the interlayer hole transfer for the first time, not only enriching the knowledge of the underlying microscopic mechanisms, but also providing instructive guidance to practical van der Waals optoelectronic devices.

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The electronic friction effects of strongly correlated systems

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We present the electronic friction of strongly correlated systems (using Hubbard model as an example) as a function of x according to mean field theory (MFT), exact diagonalization (ED) and density matrix renormalization group (DMRG). The system exists two levels due to the electron-electron interactions, so there are two peaks in the electronic friction at the resonances of electron attachment or detachment with the Fermi level of the metal. However, compared with free electron systems, the absolute values of the energy level of impurity are usually greater than the Fermi level when resonances occur, which may be induced by strongly correlated effects. Although MFT predict the two peaks, it cannot derive the accurate magnitudes and positions of peaks. The results calculated by ED show that the number of sites has important effects to the magnitudes of peaks, and also affects the positions. We further calculated the electronic friction according to DMRG for large systems. The above results indicate that as the temperature decreases, the distance between the two peaks increases; as the temperature decreases from 0.1 to 0.01, the magnitudes of peaks increase.

Photo-induced dynamics with continuous and discrete quantum baths

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The ultrafast quantum dynamics of photophysical processes in complex molecules is an extremely challenging computational problem with a broad variety of fascinating applications in quantum chemistry and biology. Inspired by recent developments in open quantum systems, we introduce a pure-state unraveled hybrid-bath method that describes a continuous environment via a set of discrete, effective bosonic degrees of freedom using a Markovian embedding. Our method is capable of describing both, a continuous spectral density and sharp peaks embedded into it. Thereby, we overcome the limitations of previous methods, which either capture long-time memory effects using the unitary dynamics of a set of discrete vibrational modes or use memoryless Markovian environments employing a Lindblad or Redfield master equation. We benchmark our method against two paradigmatic problems from quantum chemistry and biology. We demonstrate that compared to unitary descriptions, a significantly smaller number of bosonic modes suffices to describe the excitonic dynamics accurately, yielding a computational speed-up of nearly an order of magnitude. Furthermore, we take into account explicitly the effect of a δ-peak in the spectral density of a light-harvesting complex, demonstrating the strong impact of the long-time memory of the environment on the dynamics.

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TD-DMRG Study of Exciton Dynamics with both Thermal and Static Disorders for Fenna-Matthews-Olson Complex

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Photosynthesis is a fundamental process that converts solar energy into chemical energy. Understanding the microscopic mechanisms of energy transfer in photosynthetic systems is crucial for the development of novel optoelectronic materials. Simulating these processes poses significant challenges due to the intricate interactions between electrons and phonons, compounded by static disorder. In this work, we present a numerically nearly exact study using the time-dependent density matrix renormalization group (TD-DMRG) method to simulate the quantum dynamics of the Fenna-MatthewsOlson (FMO) complex considering an eight-site model with both thermal and static disorders. We employ the thermo-field dynamics formalism for temperature effects. We merge all electronic interactions into one large matrix product state (MPS) site, boosting accuracy efficiently without increasing complexity. Previous combined experimental and computational studies indicated that the static disorders range from 30 to 90 cm^{-1} for different FMO sites. We employ a Gaussian distribution and the auxiliary bosonic operator approach to consider the static disorder in our TD-DMRG algorithm. We investigate the impact of different initial excitation sites, temperatures, and degrees of static disorder on the exciton dynamics and temporal coherence. It is found that under the influence of the experimentally determined static disorder strength, the exciton population evolution shows a non-

negligible difference at zero temperature, while it is hardly affected at room temperature.

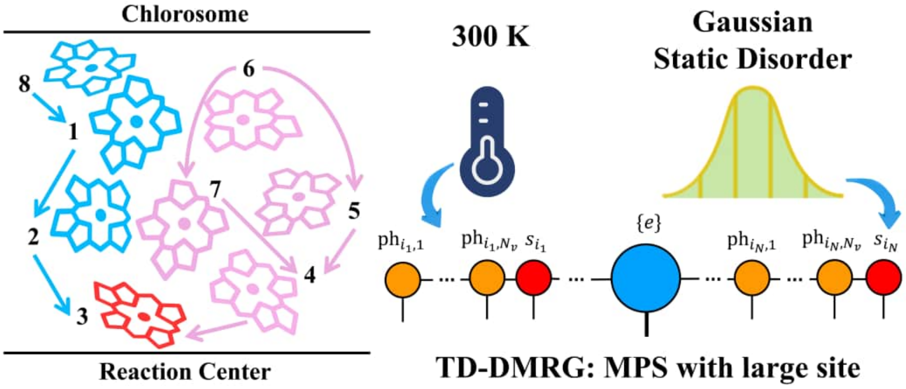

Figure 1. Exciton transport path in eight-site FMO model and TD-DMRG algorithm with large site MPS considering both thermal and static disorders.

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Theoretical Calculation of Organic Host-Guest Doped Materials with Room Temperature Phosphorescence

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Organic materials with room-temperature phosphorescence (RTP) have shown great potential in many fields. Compared to single-component counterparts, organic host-guest RTP materials composed of two non-phosphorescent compounds exhibit better luminescence properties and thus gain broad attention in recent years. [1-2] However, luminescence mechanisms of such host-guest materials are largely unclear, primarily due to difficulties in experimentally determining the exact doping structures/modes between two components. To address this issue, quantum chemical simulation as complement to experimental characterization can be employed to predict doping structures as well as uncover the intrinsic mechanisms behind luminescence phenomenon of these materials. As such, in the present work, the luminescence mechanisms of a group of host-guest materials, isoquinoline derivatives (guests) and benzophenone (host) doped systems, have been studied theoretically. The most important step in the simulation is to construct rational chemical models of the host-guest materials.

The models are generated in three steps. Firstly, we replace one host molecules by the guest molecules in the bulk of benzophenone to generate the initial doped systems. Then, various doped crystal structures are predicted by simulated annealing molecular dynamics simulations. Finally, cluster models are constructed and optimized using QM/MM methods based on the structures by simulated annealing. After that, various luminescence properties using optimized-embedded cluster models are computed at TDA-DFT level, including excitation energies, spin-orbit coupling (SOC), etc. Our results are consistent with the experimental results and demonstrate the rationality of the models.

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Hierarchical Approximation and Question-Driven Strategy for Efficient Computation of Charge Transport in Molecular Devices

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The fully self-consistent Non-Equilibrium Green's Function (NEGF) method [1], grounded in ab initio calculations, is widely used for investigating charge transport in molecular junctions with atomic-level precision. Despite its accuracy, this method's substantial computational demands, stemming from the comprehensive calculations required for all device components, pose challenges when simulating junctions with complex molecular structures and elucidating the functionality of molecular devices [2]. Conversely, theoretical descriptions based on Landauer's physical models, which consider individual electronic states and their interactions with electrodes, better captures the core principles in charge transport and reveal the underlying physical mechanisms at minimal computational cost [3], while it often lacks the detailed chemical characterization of the system.

To bridge these gaps, we propose an efficient computational strategy that employs hierarchical approximations for the molecule, the electrode, and the molecule-electrode interface, by utilizing appropriate system size definitions, Hamiltonian representations, and self-energy treatments. Driven by research objectives, this strategy suggests suitable simplifications and computational accuracies at each hierarchical level, achieving highly efficient computation of charge transmission for benchmark studies across a range of practical molecular junction systems as documented in the literature. This Question-Driven Hierarchical Computation (QDHC) strategy balances computational efficiency with accuracy, thereby providing a robust framework for analyzing charge transport mechanisms in molecular devices.

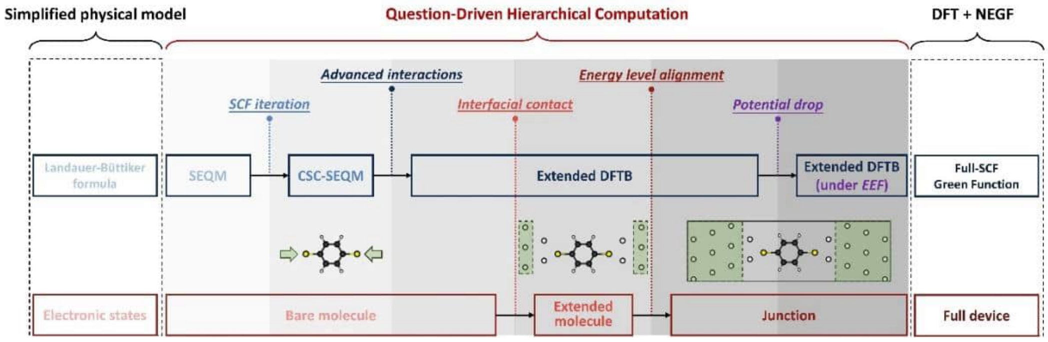

Figure 1. Framework of Question-Driven Hierarchical Computation strategy

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Activation volume in mechanochemistry: A theoretical formulation and its implication

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Activation volume emerges as a pivotal concept within the realm of nanotribology, playing a decisive role in shaping the response of interfacial bond formation/breaking reaction rates to applied mechanical force. Currently, activation volume primarily functions as a fitting parameter in reaction-rate theory, presenting a formidable challenge in fully grasping its physical connotations and theoretical computation. In this study, we introduce the innovative concept of inherent stress difference between initial and transition states, originating from the displacement of reacting atoms. Through this introduction, we unveil a universal formula for activation volume. This formula distinctly elucidates the physical significance of activation volume, representing the volume change from initial to transition states. Subsequently, our first-principles calculations of a dehydration bonding reaction system at silica/silica interface successfully validate the proposed activation volume formula across a spectrum of reactions. In summary, this work provides a lucid physical depiction of activation volume and its computational methodology, making a substantial contribution to the foundational understanding of mechanochemical reactions and advancing the field.

Design of Bipolar Organic Matrices for Rechargeable Redox Reactions in Non-Aqueous Electrolytes

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Organic electrode materials (OEMs) combine high-energy density with cost-effectiveness and environmental compatibility which makes them currently a target of intense research. Depending on the ease of reduction and oxidation, OEMs are used either as cathodes or as anodes in metal-ion batteries but the bipolar OEMs contain both reducible and oxidizable fragments and thus can serve as symmetric electrodes.

Naphthalimide derivatives occupy a special place among OEMs due to their intriguing redox–switchable properties [1]. Recently, peri-disulfo derivatives were synthesized and tested as successful bipolar OEMs for Li-ion batteries [2]. Given that selenium is a better nucleophile than sulfur [3], peri-diselenolo analogues were designed and their implementation in electrochemical cells with LiTFSI in ionic liquid as electrolyte was analyzed both experimentally (by *ex-situ* XRD, SEM/EDS and EPR analyses) and computationally (by means of molecular modelling with DFT). Structural, electronic and electrochemical characteristics were quantified to supplement and interpret the experimental findings. Comparison with the performance of previously designed coordination polymers is made.

The research was funded by the Bulgarian Science Fund, project CARiM/VIHREN, КП-06-ДВ-6/2019 and project КП-06-Н69/1/2023.

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Device engineering optimization of organic photovoltaic assisted by machine learning

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Device engineering is a key link in determining the performance of organic photovoltaic (OPV). How to efficiently optimize OPV device engineering to maximize the theoretical performance limit of photoactive materials is a major bottleneck in the development of this field. To this end, based on large-scale experimental/theoretical data, and combining quantum chemistry and machine learning, the potential correlation between organic photoactive materials, important device engineering parameters and photovoltaic performance, as well as the quantitative structure-property relationships of OPV systems are systematically investigated. Moreover, the device engineering parameters of potentially unexplored materials are reverse-optimized using the constructed theoretical model. Through the data- and computation-driven research mode, the favorable range of device process parameters values for new photoactive materials can be efficiently discovered before the experiment, which is of great significance for the practical development of high-performance OPV.

Theory of Electron Spin Resonance Spectroscopy in Scanning Tunneling Microscopy

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The integration of scanning tunneling microscopy (STM) and electron spin resonance (ESR) spectroscopy has emerged as a powerful and innovative tool for discerning spin excitations and spin-spin interactions within atoms and molecules adsorbed on surfaces. However, the origin of the STM-ESR signal and the underlying mechanisms that govern the essential features of the measured spectra have remained elusive, thereby significantly impeding the future development of the STM-ESR approach. Here, we construct a model to carry out precise numerical simulations of STM-ESR spectra [1,2] for a single hydrogenated Ti adatom and a hydrogenated Ti dimer, achieving excellent agreement with experimental observations. We further develop an analytic theory that elucidates the fundamental origin of the signal as well as the essential features in the measured spectra. These new theoretical developments establish a solid foundation for the on-demand detection and manipulation of atomic-scale spin states, with promising implications for cutting-edge applications in spin sensing and quantum computing.

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Modelling the emissive properties of NIR-emitters

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In this study, we conducted a comprehensive computational investigation into the emissive properties of a series of representative near-infrared (NIR) luminescent materials. The molecular systems studied include various structures (Figure 1): compounds 1-3 are flavylium polymethine derivatives with different substituents, compounds 4 and 5 vary in conjugation length (odd versus even numbers), and compounds 6 and 7 feature symmetrical versus asymmetrical configurations. Utilizing in-house computational protocols, we calculated vertical emission energies for the first bright electronic state, as well as radiative and non-radiative decay rates, through time-dependent density functional theory (TD-DFT) and vibronic calculations. Additionally, we computed the inner reorganization energies and fluorescence quantum yields (FQY) of these molecules. By comparing the computational results with experimental data, we identified key parameters that show a strong agreement with experimental observations. Notably, our analysis revealed that molecules with an even number of double bonds and symmetrical structures possess lower inner reorganization energies and higher FQYs, indicating enhanced photophysical performance.

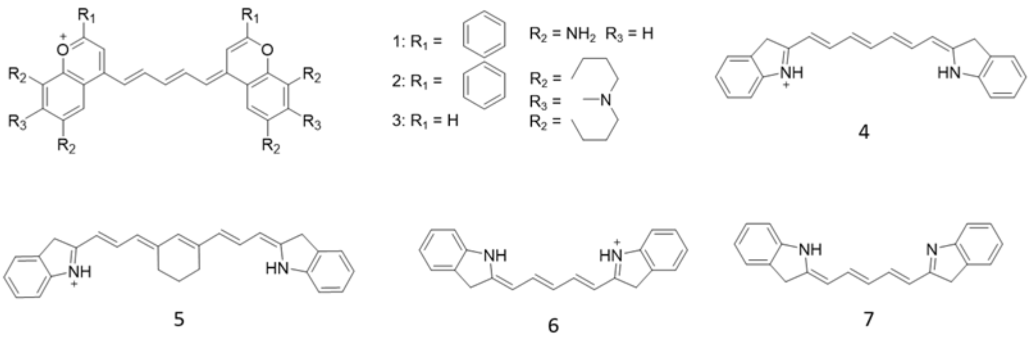

Figure 1. The chemical structure of the NIR investigated molecules.

Simultaneous Intra- and Intermolecular Singlet Fission Through Macrocyclic Structures

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Singlet fission (SF) is a down-conversion photophysical process involving transforming a high-energy singlet state into two lower-energy triplet excitons. It has attracted extensive attention over the past two decades due to its potential to break the power conversion limit in photovoltaic devices. Typically, ultrafast singlet fission occurs through intermolecular processes (xSF), but precisely controlling molecular packing in experiments is challenging and is further complicated by defects, crystallinity, and morphology. In contrast, intramolecular singlet fission (iSF) materials allow for fine-tuning their electronic structure through different bridging groups. However, the question of how to design these bridging groups rationally to maintain the proper interaction between chromophores is worth exploring.

In this study, we propose a novel SF molecular design strategy: employing a macrocyclic structure to maintain π-π packing between two pentacene units and optimize through-space interactions, using the inherent molecular control advantages of iSF to address the challenges of controlling packing in xSF. Before designing the bipentacene macrocycle, it is necessary to understand how iSF occurs within macrocycles and what drives it. Considering that the active layer of solar cells usually employs films rather than solutions, it's crucial to explain the aggregation behavior of SF molecules in the solid state and its impact on SF dynamics. However, the SF dynamics in films or concentrated solutions can become complex as intra- and intermolecular SF may occur. This work combines various theoretical calculation methods, including density functional theory, multi-reference wave function methods, and molecular dynamics, to study and reveal the iSF mechanism of bipentacene macrocycles in dilute solutions, clarify the aggregation behavior of bipentacene macrocycles in concentrated solutions or films and their iSF/xSF behavior, and then design a series of efficient SF bipentacene macrocycles. This study provides a theoretical foundation for the design of future iSF materials and the development of SF-based photovoltaic devices.

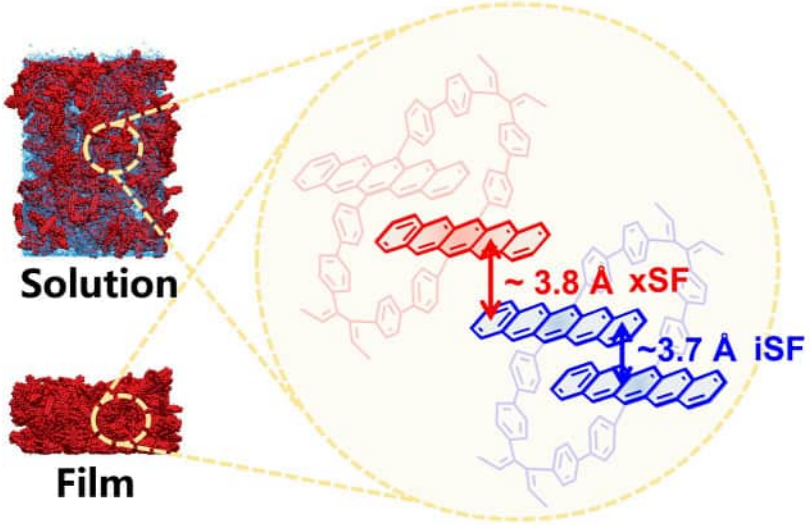

Figure 1. Simultaneous Intra- and Intermolecular Singlet Fission in Bipentacene Macrocycle Aggregates

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PM6/L8-BO Thin Films through Layer-by-Layer Engineering: Formation Mechanism, Energetic Disorder, and Carrier Mobility

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Layer-by-layer (LBL) process has emerged as a promising method in the advancement of organic photovoltaics (OPVs), emphasizing scalability and reproducibility. More importantly, it provides enhanced morphological control for boosting carrier mobility (μ) and power conversion efficiency (PCE). By employing a multiscale approach that combined first-principles calculations, molecular dynamics simulations, and kinetic Monte Carlo methods, we elucidated the relationship between LBL morphology engineering and carrier mobility in donor/acceptor (PM6/L8-BO) thin films. During solvent evaporation, the order of solid-phase formation in LBL films was top surface, bottom region, and then the middle region. The early solid precipitation from precursor solutions was acceptor, resulting in a well-ordered molecular arrangement and reducing energy disorder of acceptor LUMO levels. Furthermore, the difference in energy disorders between the A/D blend region and the pure A or D domains enabled LBL morphology engineering to balance electron and hole mobilities, thereby mitigating charge accumulation and recombination. LBL-manufactured films presented higher carrier mobility ($\mu_e^{\mathrm{LBL}} = \mu_h^{\mathrm{LBL}} = 1.9\times10^{-3}$ $\mathrm{cm^2\cdot V^{-1}\cdot s^{-1}}$) compared to bulk heterojunction (BHJ) films ($\mu_e^{\mathrm{BHJ}} > \mu_h^{\mathrm{BHJ}} = 0.1\times10^{-3}$ $\mathrm{cm^2\cdot V^{-1}\cdot s^{-1}}$). These mechanisms provided insights into strategies for enhancing charge extraction of photo-generated charge carriers through LBL engineering, driving the development of efficient OPV materials.

Machine learning-assisted dual-atom sites design with interpretable descriptors unifying electrocatalytic reactions

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This work describes an interpretable descriptor model to unify activity and selectivity prediction for multiple electrocatalytic reactions (i.e., O_2/CO_2/N_2 reduction and O_2 evolution reactions), utilizing only easily accessible intrinsic properties. This descriptor, named ARSC, successfully decouples the atomic property (A), reactant (R), synergistic (S), and coordination effects (C) on the *d*-band shape of dual-atom sites, which is built upon our developed physically meaningful feature engineering and feature selection/sparsification (PFESS) method. We can rapidly locate optimal catalysts for various products instead of over 50,000 density functional theory calculations. The model's universality has been experimental validated. This work opens the avenue for intelligent catalyst design in high-dimensional systems linked with physical insight [1].

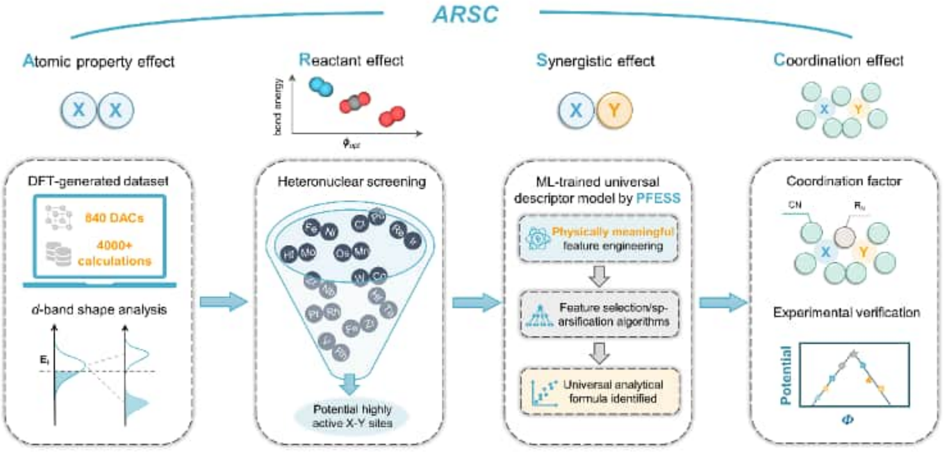

Figure 1. General workflow of our work.

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DPA-Semi:Machine-Learning-Based Interatomic Potentials for Group IIB to VIA Semiconductors: Towards a Universal Model

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Machine-learning-based interatomic potentials have become powerful tools for simulating large systems with ab initio accuracy. However, a universal model for various materials is still needed. We introduce the DPA-Semi model[1], a unified deep-learning potential trained on DFT data for 19 semiconductors ranging from groups IIB to VIA, including Si, Ge, SiC, BAs, BN, AlN, AlP, AlAs, InP, InAs, InSb, GaN, GaP, GaAs, CdTe, InTe, CdSe, ZnS, and CdS. Independent models for each semiconductor were also prepared. We systematically compare the structural, electronic, and thermodynamic properties of solid and liquid phases across different machine-learning models. Our results show that the DPA-Semi model achieves GGA-level accuracy and can be regarded as a pre-trained model towards a universal semiconductor model for group IIB to VIA materials.

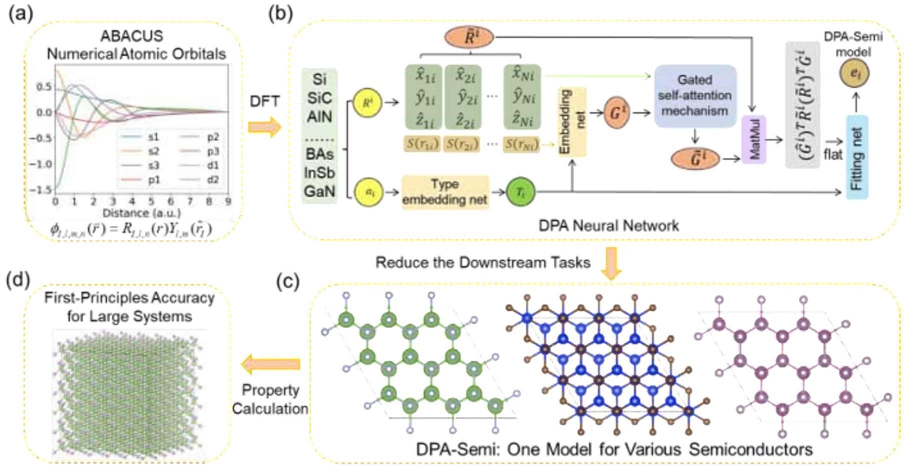

Figure 1. Development process of the DPA-Semi model: (a) Generate atomic datasets with ABACUS using NAO basis sets; (b) Train the DPA-Semi model via a gated self-attention mechanism using DFT datasets; (c) Apply DPA-Semi to various semiconductors, reducing computational costs; (d) Use DPA-Semi for large-system property calculations with GGA-level accuracy.

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Machine learning-aided in-situ structure identification of low-dimensional carbon nanomaterials from STM images

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Scanning tunneling microscopy (STM) provides atomic-level resolution of solid surfaces, nanomaterials, and molecular systems, offering unique insights into their geometric and electronic structures[1]. Thereinto, the research of graphene related low-dimensional carbon nanomaterials using STM has caused widespread interests [2,3]. However, the structural complexity of carbon conjugated system makes traditional STM image analysis both time-consuming and error-prone. This highlights the need for an advanced framework capable of swiftly and accurately discerning these intricate structures, thereby improving the efficiency and reliability of STM-based research. Here, we adopted a state-of-the-art machine vision algorithm to facilitate the rapid identification of carbon conjugated structures from STM images. The model was trained on a comprehensive dataset comprising nearly 50,000 molecules and 700,000 theoretical STM images, aiming to translate STM images into annotated representations of atomic positions. We integrated this model directly into the STM measurement, enabling in-situ detection and identification of various carbon nanostructures synthesized on surfaces. This algorithm marks a significant advancement in aotomated STM analysis, accelerating the discovery of complex nanostructures and enhancing the automation of surface science research.

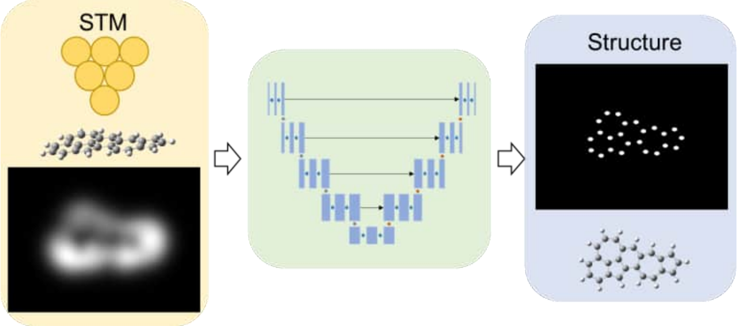

Figure 1. Automated STM analysis accelerates in-situ identification of complex carbon nanostructures.

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Predicting Regioselectivity in Functionalized Fullerenes and Carboncones Using Deep Learning

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Carboncones and fullerenes are renowned for their π-conjugated, positively curved surfaces, which facilitate the attachment of various atoms and functional groups. However, the complexity of predicting addition patterns poses a significant challenge due to the intricate regioselectivity exhibited by these materials [1]. In this contribution, we present an innovative incremental deep learning approach to predict regioselectivity in atomic additions to carboncones and fullerenes [2]. Our deep neural network (DNN) models utilize graph-based features, relying solely on atomic connectivity without the need for 3D molecular coordinates or iterative optimization. This approach circumvents the risk of producing chemically unreasonable structures, particularly in highly distorted adducts. Our DNN models accurately predict regioselectivity in hydrogenated carboncones of $C_{70}H_{20}$ and $C_{62}H_{16}$, accommodating up to 40 and 30 additional hydrogen atoms, respectively. Moreover, the model successfully predicts experimental addition patterns in $C_{50}Cl_{10}$ and $C_{76}Cl_n$ (n = 18, 24, and 28), outperforming all other known methods. The predictive power and generalization ability of our approach represent a significant advancement over previous methods, making it a powerful tool for exploring complex addition patterns in carbon nanomaterials.

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Active Learning for Fast and Robust Dynamics Simulations

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Quantum mechanical calculations can be greatly accelerated by machine learning potentials (MLPs) [1], where the sampling of points on the potential energy surface (PES) can affect the accuracy of the MLPs [2]. As a result, several active learning schemes have been developed that use geometrical or statistical sampling criteria [2]. Here we introduce the data-efficient active learning that produces robust machine learning potentials by automatic sampling of the data [3]. Our implementation allows us to perform simulations on commodity hardware with affordable time investment and minimum human interference. Our active learning scheme is robust and general enough as we showed in several application scenarios, e.g., vibrational spectra simulation, conformer search, and reaction mechanism elucidation. Our calculations were done with MLatom [4] that can be also used online at https://XACScloud.com.

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Stability Prediction of Gold Nanoclusters with Different Ligands and Doped Metals by Deep Learning

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The stability and experimental accessibility of gold nanoclusters, modulated by various ligands and doped metal atoms, are crucial prerequisites for their potential applications across energy materials, catalysis, sensors, bio-imaging, and therapy. To effectively screen stable candidates from the intricate combination space formed by different metal cores and ligands, predicting the stability of Au nanoclusters before experimental synthesis is necessary. A comprehensive dataset is established by determining the formation energies (E_{form}) of diverse Au nanocluster structures, encompassing 21 distinct core sizes, 22 types of ligands, and 7 varieties of doped metal atoms, through density functional theory (DFT) calculations. [1] Deep learning techniques, specifically the graph convolutional neural network (GCNN), is found to be effective in predicting formation energies of Au nanoclusters. The efficiency of deep learning model is further supported through external test sets, which include synthesized nanoclusters of particular interest due to their responsiveness to stimuli and biocompatibility. The predictive power of the deep learning model also facilitates the successful synthesis of novel structures, such as $Au_{10}(PPh_3)_7Cl_3$ and $Au_{38}OT_{24}$ (OT = octane-1-thiol), with predicted formation energies closely matching those of known nanoclusters. This proposed machine learning approach holds considerable promise in expediting the high-throughput discovery and synthesis of nanoclusters in experiment.

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UAIQM – the New Generation of Universal AI Models

Yuxinxin Chen,[1] Yi-Fan Hou,[1] Olexandr Isayev,[2] Pavlo O. Dral[1*]

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Neither traditional QM methods nor state-of-the-art AI models can successfully solve the dilemma between accuracy and cost on their own and the selection of a suitable method often require human expertise. Thus, we propose a paradigm shift from a single QM or AI method to an online platform where a library of general-purpose methods, which we named **UAIQM** (**U**niversal and **U**pdatable **A**rtificial **I**ntelligence-Enhanced **Q**uantum **M**echanical Foundational Models), is hosted [1]. Given the chemical system and resources available, the best solution can be provided. Moreover, our library is continuously improved with the joint effort of the community and users worldwide. We demonstrate that UAIQM enables accurate and fast simulations of reaction barriers, energetics, infrared spectra, etc. Calculations with UAIQM can be done using MLatom [2] at https://XACScloud.com.

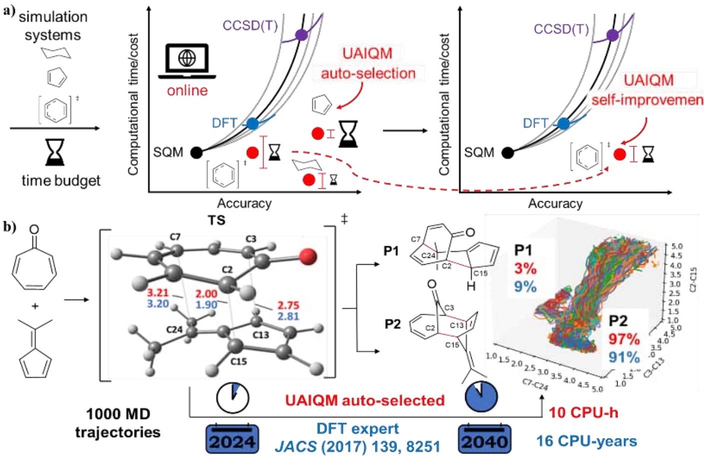

Figure 1. a) New paradigm. b) Simulating bifurcating reaction with UAIQM.

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Performance prediction for all small-molecule-based organic solar cells

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A large database of small molecule OSC containing their experimental characteristics and a broad set of computed properties was constructed.[1] Also, a method based on a leave-one-group-out cross-validation, in which an ML model to accurately perform extrapolations on unseen families of compounds was proposed.[2] Besides, ML models of predicting properties, screening candidates, and optimizing devices discussed in OSC systems were summarized.[3] Moreover, a donor and acceptor pairwise molecular embedding representation algorithm is proposed and packaged into a tool for ML modeling power conversion efficiency of OSCs.[4] In addition, the database (Figure 1) of all small-molecule-based organic solar cells has been updated for further ML works in OSC systems.

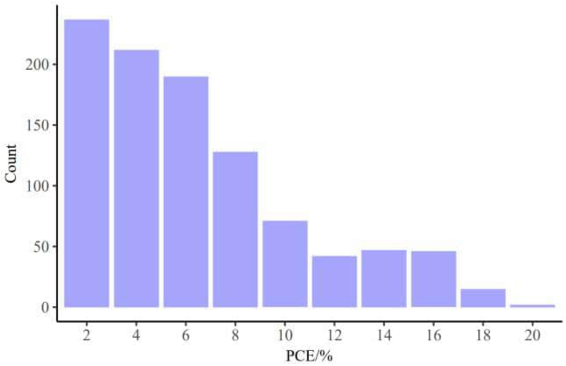

Figure 1. The database for all small-molecule-based organic solar cells

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DC-PUHF: Toward large-scale quantum chemical calculation including static correlation

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1. Introduction

Various large-scale quantum chemical calculation methods have been developed so far. In particular, large-scale correlation methods are important for the quantitative description of chemical reactions. However, previous studies mainly focus on dynamical correlation (e.g. Møller-Plesset and coupled-cluster theories), and their extensions to static correlation theories remain frontier. Scuseria group has developed the projected UHF (PUHF) method[1], which extracts a pure spin state of interest from the UHF wavefunction. This method opens up the possibility of treating static correlation in a more transparent manner.

We have applied the divide-and-conquer (DC) method, one of the linear scaling schemes, to various calculation methods[2]. This study aims to apply the DC scheme to the PUHF method and to enable large-scale static correlation calculation.

2. Theory

In the DC method, a system is divided into subsystems, and eigenvalue problems for each subsystem are solved. The total density/Fock matrix is constructed from subsystem ones. We applied the total density/Fock matrices obtained by the DC scheme to the projection scheme. We implemented the DC-PUHF method into the modified version of the GAMESS program.

3. Result

The figure shows the potential energy curves of poly-(phenoquinodimethane) (n=10) over the dihedral angle. The DC-PUHF method can reproduce the PUHF result when adopting sufficient buffer size.

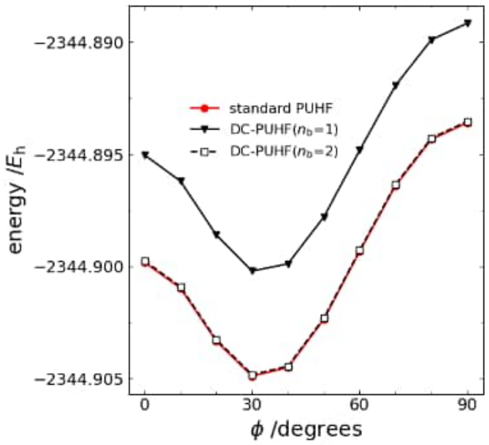

Figure. Potential energy curve for p-PQDMs (n=10) to the dihedral angle.

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Accurate and efficient CCSD(T)/CBS: development and application for complicated molecules up to 1000 atoms

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Our recent development efforts[1,2] and large-scale applications[3,4] are presented, illustrating the accuracy and efficiency of the local natural orbital (LNO) coupled-cluster (CC) family of methods. We implemented highly-optimized and parallel closed- and open-shell, linear-scaling MP2, LNO-CCSD(T) [1] and general-order LNO-CC in the MRCC program suite, www.mrcc.hu [2].

The accuracy of the LNO and AO basis convergence can be systematically improved and extrapolated toward the canonical CCSD(T)/CBS limit, also yielding robust uncertainty estimates.[1,3] We also developed a general floating Gaussian (FOG) basis approach, bringing the cost of the CBS limit ca. one cardinal number lower [2b].

In all existing, mostly independent comparisons of popular local CCSD(T) variants covering energetic properties of ca. 1000 systems in 14 test sets (reviewed in [3]), LNO-CCSD(T) was found to be the most accurate. Since LNO-CCSD(T)/CBS(T,Q) usually takes about an order of magnitude more time than HF/CBS(T,Q), it is affordable also in protocols using hybrid DFT, e.g., for structures, vibrations, etc. The exceptionally low minimal memory and disk requirement (few tens of GBs) of the LNO method make it routinely applicable for molecules of a few 100 atoms even with a single CPU.[1,3]

Our recent LNO-CCSD(T) applications of unique accuracy over cost performance include: challenging supramolecular complexes[4a], matching CC with experiments for CO adsorbed on MgO surface[4b], and enzyme catalysis/protein interactions up to 1000 CC-level atoms.[1,3] We recently reviewed the state of local CC methods[3] including 50+ advanced LNO-CCSD(T) applications for realistic, large systems across main group, transition metal, bio-, and surface chemistry.

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Accurate Chemical Reaction Modeling on Noisy Intermediate-Scale Quantum Computers Using a Noise-Resilient Wavefunction Ansatz

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Quantum computing holds great potential for simulating chemical systems. In this study, we propose an efficient protocol for quantum computer-based simulations of chemical systems, enabling accurate chemical reaction modeling on noisy intermediate-scale quantum (NISQ) devices. In this protocol, we combine a correlation energy-based selection to define the active space, the driven similarity renormalization group (DSRG) method to account for the electron correlation effect, and a noise-resilient wavefunction ansatz to mitigate errors. This combination provides a quantum resource-efficient way to accurately simulate chemical systems. The power of this protocol is demonstrated by numerical results for systems with up to tens of atoms. Additionally, modeling a Diels-Alder (DA) reaction using this protocol is performed on a cloud-based superconducting quantum computer. These results represent an important step forward in realizing quantum utility in the NISQ era.

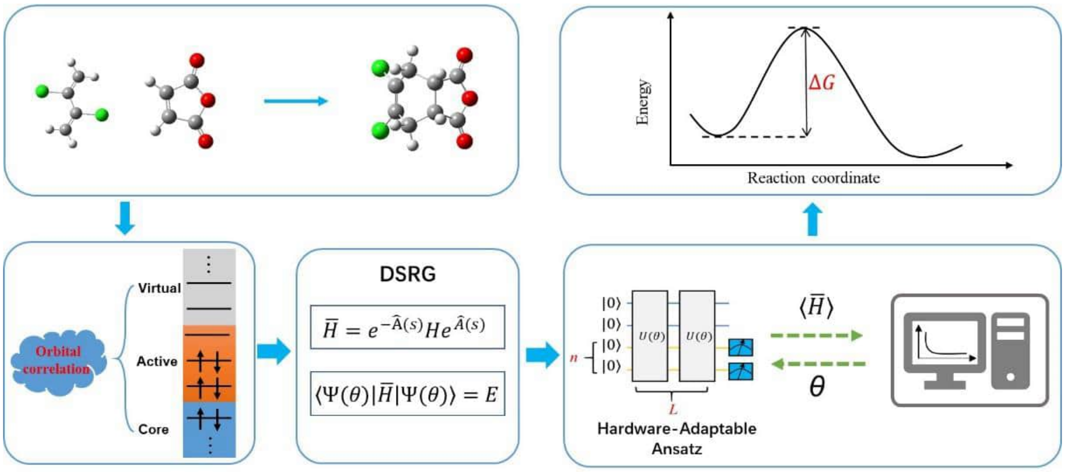

Figure 1. Workflow of the hybrid quantum-classical algorithm

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Variational quantum computation for large molecules using matrix product state inspired ansatz

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Variational quantum eigensolver (VQE) has been successfully applied in quantum chemistry applications, while conventional VQE ansatzes require a large number of qubits exceeding the capacity of current NISQ devices. In this research[1], we proposed to use the recently developed quantum circuit matrix product state (QCMPS) ansatz[2] to simulate large molecules in a qubit-efficient way. Adopting a fully-entangled circuit structure in combination with proper orbital localization, QCMPS reaching comparable accuracies with DMRG using only a maximum number of 6 qubits in simulating the ground state of linear hydrogen chain with up to 50 orbitals. The QCMPS ansatz presented in this study provides an promising way to perform quantum simulations for large-scale molecular systems with limited qubit resources.

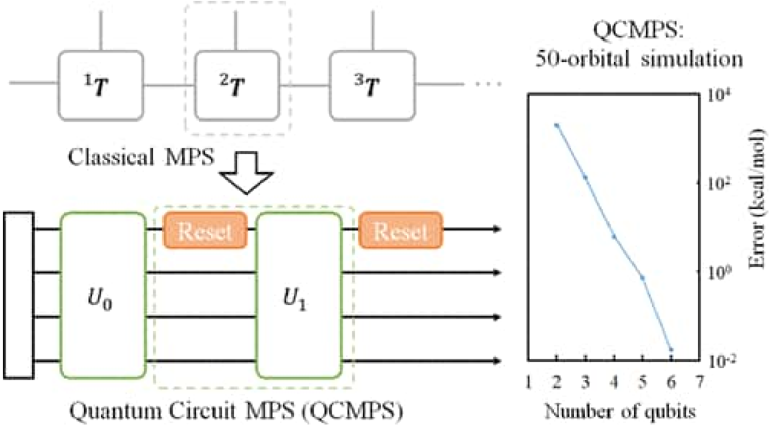

Figure 1. A schematic graph of QCMPS ansatz.

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Quantum Equation-of-Motion Method with Triple Excitations Reduced by Perturbation and Symmetry

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According to the development of quantum computer and the notable achievements of the equation-of-motion (EOM) [1] method, the quantum EOM (qEOM) [2] method has been proposed for the study of electronically excited states. However, the standard qEOM method, which includes only single and double excitations, struggles to accurately describe states that are primarily influenced by double excitations. To overcome this limitation, we first reformulate the qEOM method using an effective Hamiltonian framework and then introduce an optimized implementation that incorporates single, double, and triple excitations (qEOM-SDT). By applying point group symmetry and perturbation theory, we achieve a significant reduction in the number of triple excitations. Additionally, a perturbative correction is applied to account for the impact of the omitted triple excitations on excitation energies. Our method demonstrates energy deviations of less than 0.18 eV while requiring fewer than 9% of the triple excitations for complex cases, such as the $2^1\Delta$ state of CH^+ and the $2^1\Sigma$ state of HF. Furthermore, we extend the operator screening approach to the quantum subspace expansion method for the computation of excitation energies.

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Quantum structure search for molecular ground-state energy computation

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This paper explores a novel approach to extend the natural architecture search algorithm (NAS) from the classical machine learning domain to quantum circuits, for finding a universal quantum circuit capable of computing the ground-state energy of molecules. Initially, a universal set of quantum gates is constructed, comprising the types of gates used in the ansatz typically employed for computing the ground-state energy of molecules. Analogous to the training set in machine learning, we construct a set of quantum gates from these gates and search for quantum circuits using three methods: Monte Carlo algorithm, random algorithm, and genetic algorithm. Our goal is to apply the obtained circuits to several typical chemical systems, and after computation using the variational quantum eigensolver (VQE) algorithm, obtain ground-state energy solutions close to full configuration interaction (FCI). We also study further optimization of circuits by adding ancillary qubits. The research findings indicate that when circuits obtained through genetic algorithm search are augmented with an appropriate number of ancillary qubits, optimal results in terms of circuit depth and entanglement (measured by the number of CNOT gates) are achieved. These results demonstrate that our method not only exhibits good scalability but also facilitates parameter optimization, offering new insights and approaches for the application of quantum computing in chemical calculations.

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A Hybrid Framework for Simulating Molecular Systems on Quantum Computers

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Simulating the electronic structure of molecules on real quantum devices remains very challenging. We propose a hybrid quantum-classical framework for the simulation of molecular systems. It is realized by combining the variational quantum eigensolver (VQE) with multi-state density functional theory (MSDFT) [1], but is flexible to incorporate other SCF approaches. Furthermore, we put forward two techniques to address the critical challenges associated with hardware imperfection. First, a way of partitioning quantum circuits is designed to characterize the static correlation between different electronic configurations, so as to scale up the capacity of active space. Second, a DFT correlated error mitigation method is developed, which contributes to a high-precision illustration about dynamic correlation. The utility of our framework is evaluated on molecular systems of interest via the computation of bond breaking, intrinsic reaction coordinates and conical intersections. We performed quantum simulation with up to 86 qubits on the Quafu quantum computing platform [2]. The results show that the accuracy of our approach is in close agreement with classical multi-reference methods. In addition, dynamic correlation is well treated through MSDFT and hence the approach produces lower conical intersection energy than existing hybrid quantum-classical works [3].

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Integrating Self-initialized Local Thermalizing Lindblad Operators for Variational Quantum Algorithm with Quantum Jump: Implementation and Performance

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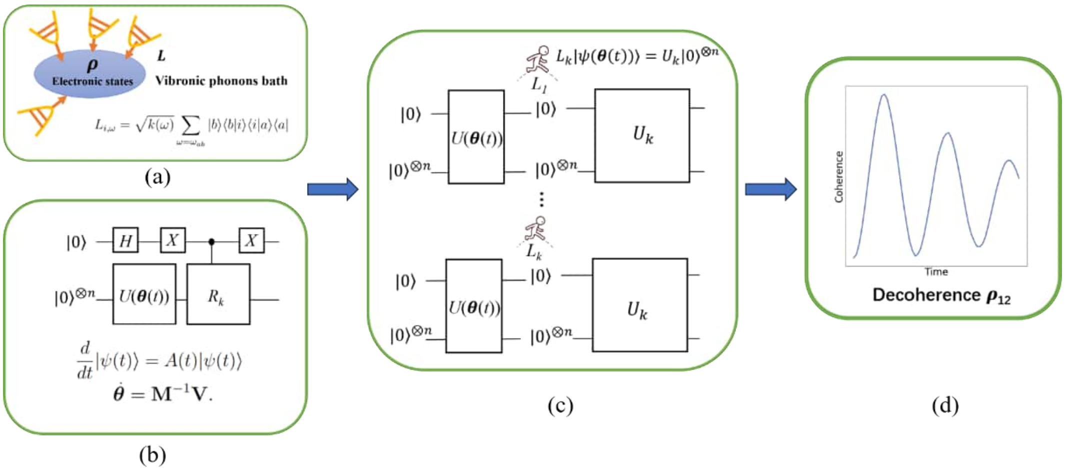
Using quantum computers to simulate quantum systems such as molecular systems is one of the most promising short-term applications of quantum computing, and the similarity between the unitary evolution of quantum circuits and the time evolution of quantum systems inspires us to simulate the dynamics of quantum systems on a quantum computing device. However, unlike the unitary evolution of a closed quantum system, the time evolution of the quantum state of the vast majority of practical open quantum systems, such as the electron-phonon coupled molecular systems, is non-unitary. This makes the evolution process difficult. Here we present a scheme, denoted as VQA-QJ-LTLTME, which adopts the trajectory average of quantum jump Monte Carlo wave function variational evolution to evolve the system's density matrix and local thermalizing Lindblad operators to describe the electron-phonon coupling effect. This combination allows the quantum circuit to be initialized after a period of evolution, thereby eliminating the accumulation of errors, and it requires only $\log_2(n)$ qubits for system size n and a time complexity of $O(Tn^3)$, indicating that it is very suitable for operation on noisy intermediate-scale quantum devices. The VQA-QJ-LTLTME algorithm has been implemented on superconductor quantum computers. To demonstrate its performance, we simulate the dynamics of two-level spin-boson model and four-level Fenna-Matthews-Olson complex systems with both quantum and classical simulators.



(a) (b) (c) (d)

Figure 1. General scheme of VQA-QJ-LTLME algorithm.

Circuit-Efficient Qubit-Excitation-based Variational Quantum Eigensolver

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Classical algorithms encounter an "exponential wall" when addressing problems in quantum chemistry, but quantum computers offer promising solutions to these challenges. One key problem in quantum chemistry is the time-independent Schrödinger equation. The Quantum Phase Estimation (QPE) algorithm is known to be exponentially faster than classical methods. However, QPE requires substantial quantum resources, which exceed the capabilities of current Noisy Intermediate-Scale Quantum (NISQ) devices.

To address this, the Variational Quantum Eigensolver (VQE), a quantum-classical hybrid algorithm, has been proposed. VQE leverages quantum computers in the NISQ era by preparing a parameterized quantum state and measuring its energy on a quantum device. A classical computer then optimizes the parameters to minimize the energy. The variational principle ensures that the calculated energy will never be lower than the ground state energy, so a lower energy approximation will be closer to the true ground state energy.

The parameterized quantum state, known as the ansatz, is crucial to VQE. The ADAPT-VQE algorithm provides a systematic framework for constructing the ansatz from a predefined pool of operators. The performance of the ansatz heavily depends on this operator pool. Some pools, like FEB and QEB, converge quickly but require substantial quantum resources. Others, such as QCC and qubit-ADAPT-VQE, are more resource-efficient but converge more slowly.

Here, we propose a new operator pool that balances resource efficiency with rapid convergence, marking a significant step toward the effective utilization of NISQ devices.

Kylin-V: An Open-source Package Calculating the Dynamic and Spectroscopic Properties of Large Systems

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Quantum dynamics simulation and computational spectroscopy serve as indispensable tools for the theoretical understanding of various fundamental physical and chemical processes, ranging from charge transfer to photophyscical and chemical reactions. When simulating realistic systems, the main challenge arises from the huge number of degrees of freedom and the many-body correlations. Here, we present Kylin-V, an innovative quantum dynamics package designed for accurate and efficient simulations of dynamics and spectroscopic properties of vibrational systems with tensor train (TT). For qunatum dynamics, Kylin-V supports TT methods such as time-dependent density matrix renormalization group (TD-DMRG) and our recently proposed stochastic single-site (SS) [1] and hierarchical mapping (HM)[2,3] approaches. However, unlike the vibronic problems, the pure vibrational systems usually have lower excited energy and vibrational spectra requires higher resolution. Here Kylin-V supports state-average DMRG and non-TT vibrational heat-bath configuration interaction (VHCI)[4] to calculate the anharmonic frequencies and make assignments for the spectral peaks.

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Metal-Centered Boron-Wheel Cluster of Y©B_{11}^{2-} with Rare D_{11h} Symmetry

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Molecules with high point-group symmetry are interesting prototype species in textbook. As transition metal-centered boron clusters tend to have highly symmetric structures to fulfil multi-center bonding and high stability, new boron clusters with rare point-group symmetry may be viable.[1,2] Through in-depth scrutiny over the structures of experimentally already observed transition metal-centered boron-wheel complexes, geometric and electronic design principles are summarized, based on which we studied M©B_{11}^{k-} (M = Y, La; Zr, Hf; k = 1, 2) clusters and found that a Y©B_{11}^{2-} boron-wheel complex has an unprecedented D_{11h} point-group symmetry.[3] The remarkable stability of planar Y©B_{11}^{2-} complex is illustrated via extensive global-minimum structural search as well as comprehensive chemical bonding analyses. Similar to other boron-wheel complexes, the Y©B_{11}^{2-} complex is shown to possess σ and π double aromaticity, indeed following the electronic design principle previously summarized. This new compound is expected to be experimentally identified, which will extend the currently known largest possible planar molecular symmetry and enriches the metal-centered boron-wheel class.

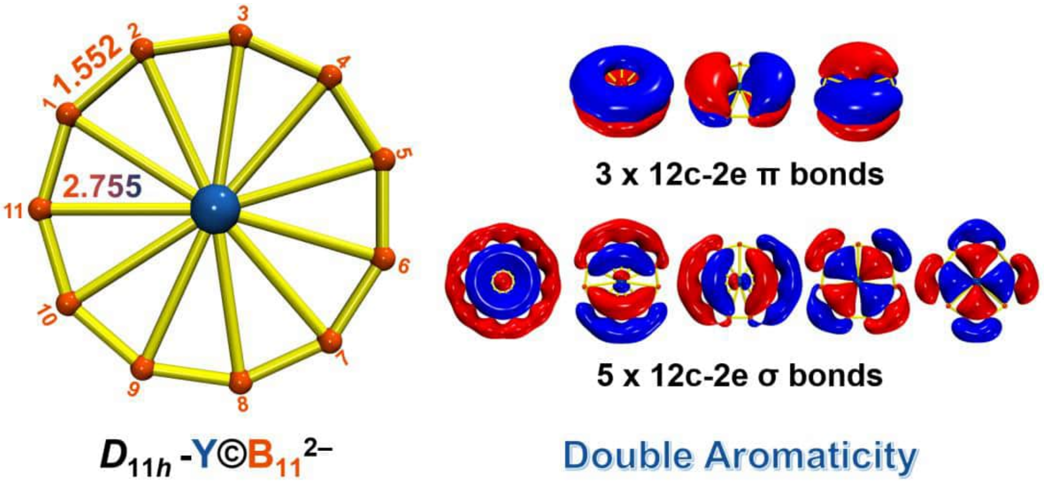

Figure 1. A schematic diagram to illustrate the electronic structure and double aromaticity of Y©B_{11}^{2-} complex briefly.

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Theoretical Studies on Strong Coupling Mechanism Between Surface Plasmon and Molecules

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The strong coupling between surface plasmons and molecules has broad applications in nanophotonics, ultrafast spectroscopy, and quantum optics. Understanding the mechanism behind this strong coupling is crucial for precise control of light-matter interactions at the nanoscale. To explore this, we employed a discrete interaction model to investigate the coupling mechanism of molecules near plasmonic nanocavities. Our results show that the coupling strength increases as the distance between molecules and nanoparticles decreases, and it is directly proportional to the electric field strength. Additionally, smaller mode volumes generate stronger near fields, further enhancing the coupling strength. Increasing the size of plasmonic nanoparticles and the number of molecules also boosts the coupling strength. However, intermolecular interactions and their impact on cavity modes may limit the extent of this enhancement. The orientation and lifetime of both molecules and plasmonic nanoparticles significantly influence the coupling strength as well. These insights are essential for designing and optimizing nanotechnological devices that rely on plasmon-molecule interactions.

Keywords: plasmons; strong coupling; discrete interaction model

Analytical Derivative Approaches for Vibro-Polaritionic Structures and Properties

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Vibro-polaritons are hybrid light-matter states that arise from the strong coupling between molecular vibrations and the electromagnetic field in an optical resonator. The study of the related phenomena has spurred the emergence of a new field, now known as polaritonic chemistry. To fully understand the precise mechanisms underpinning polaritonic chemistry and provide a deeper understanding of the underlying quantum mechanical processes, developing useful theoretical models and advanced computational frameworks to describe and predict the behavior of these hybrid states is crucial. Here we present advanced analytical energy derivative approaches within the framework of the cavity Born-Oppenheimer[1,2] density functional theory (CBO-DFT) to efficiently calculate the vibro-polaritonic spectra and explore the critical points on the cavity potential energy surface. We not only demonstrate the formulation and implementation of analytical energy gradient and Hessian as well as the infrared (IR) and Raman scattering spectral intensities into the electronic structure software package, but also proposes a classical model that helps us to understand the spectral signatures.

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Electronic Absorption and Circular Dichroism Spectra of One-Dimensional Bay-Substituted Chiral PDIs: Effects of Intermolecular Interactions, Vibronic Coupling and Aggregate Size

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Electronic circular dichroism (ECD) spectroscopy is the preferred tool for studying organic chiral supramolecules. However, it is a great challenge to experimentally clarify the contributions to ECD spectra from molecular vibrational motions and the intermolecular interactions, key factors for an efficient system architecture design of chemical sensors, catalysts or optoelectronics. Focusing on this issue, here, we perform theoretical studies on the vibrationally-resolved absorption and ECD spectra of the one-dimensional bay-substituted chiral perylene diimides (PDIs) by employing the non-Markovian stochastic Schrödinger equation (NMSSE) with respect to the model Hamiltonian in the diabatic representation, which includes the intramolecular localized excitations (LEs), inter-molecular change transfer excitations (CTEs) and the electron-vibration coupling as well. The calculated results unveil the structure-property relationship of chiral aggregates, and imply that the adopted approach can qualitatively forecast the experimentally observed spectral lineshapes. We also make a comparison among the pure electronic spectra yielded by the time-dependent density functional theory (TD-DFT) calculation and the mixed exciton model with and without the couplings between the LEs and CTEs. It is shown that the LE-CTE mixture results in the emergence of new peaks or trough in the high-energy band, and a significant deviation between the calculated ECD spectrum and that predicted by the exciton chirality rule. It is further shown that the oligomers' ECD spectra exhibit an odd-even alternation pattern with changes in aggregate size. The experimental supermolecular ECD spectra seem to be a average of the oligomers' spectra with odd and even number of PDIs.

Quantum chemical approaches based on renormalized states for strongly correlated systems

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The efficient compression of Hilbert space is one of the most crucial problems in modern quantum simulation of strongly correlated systems. One approach involves using isolated states obtained within the system, such as energetically low-lying adiabatic states, to describe the Hilbert space of the system, but without considering the interaction between the system and its environment. According to quantum information theory, Schmidt decomposition can produce two sets of the most compact states representing the bipartitioned Hilbert space (system and environment) of a particular wave function. However, such procedures require knowledge of the total wave function and are hindered by the enormous degrees of freedom in the environment. In this work, we propose performing the decomposition within a model system composed of the system of interest and a defined bath space, compressed from the real environment space, to obtain renormalized states. Two novel approaches based on this idea—renormalized-residue-based multireference configuration interaction (RR-MRCI) and block interaction product state density matrix renormalization group (BIPS-DMRG)—are proposed to achieve accurate descriptions of molecules and larger systems, including polymers and molecular aggregates, respectively. Benchmarking results across several chemical systems show that these renormalized states, which consider the effects of system-environment interaction, significantly improve Hilbert space compression compared to those isolated states, which are utilized in internally contracted MRCI (ic-MRCI) and active space decomposition (ASD)-DMRG. As a result, our methods demonstrate higher accuracy and efficiency, offering a new opportunity for the accurate description of larger strongly correlated chemical systems.

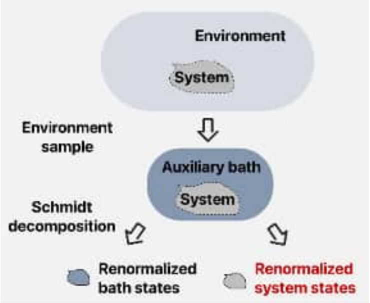

Figure 1. Schematic of obtaining renormalized system states via Schmidt decomposition in a model system composed of the system and an auxiliary bath space, which is compressed from the real environment space.

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Towards an exact description of Compound I in P450

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Studying the reactivity of Cytochrome P450 as an enzyme is crucial for understanding its functionality in metabolism [1]. Large-scale calculation beyond the density functional theory (DFT) is needed to determine its electronic structure reliably, and reactivity thereafter. Auxilary-field quantum Monte Carlo has emerged as a promising method for systems with transition metals [2, 3], in terms of efficiency and accuracy [4, 7]. In this work, we exploit the advantages of AFQMC [2, 6] and resolve an important problem in the chemistry of P450, i.e., the ground state of the iron porphyrin oxo model system, also known as Cpd I. With systematic study with respect to different hyperparameters in AFQMC, we conclude that the doublet state is the ground state, and we argue that this conclusion is unlikely to change even if one can tackle a larger active space. Furthermore, we observe that our calculation provides a A1u-A2u energy that reconciles the previous disagreements between MRCI and DFT results. These calculations highlight the importance of accurate treatment of dynamic correlation for multi-reference systems. Our work represents unprecedented many-body wavefunction calculation beyond the active space for an important multi-reference system [5] and reveals the path forward toward wide application of beyond-mean-field methods for transition metal catalysis. We also provide perspectives on the utility of fault-tolerant quantum computers for large active spaces [5].

Keywords: P450, Auxilary-field quantum Monte Carlo, Multi-reference.

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Parallel and GPU-Accelerated Implementation of Density Matrix Renormalization Group

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The density matrix renormalization group (DMRG) method is a state-of-the-art method for solving the strongly correlated systems. In this work, a parallel and GPU-accelerated implementation is developed. The parallelization focuses on the parallelism over tensor network, which can achieve a good parallel efficiency, shown as Fig.1 (a). To implement the GPU acceleration, specialized CUDA kernel function for three matrices multiplication (3MM) is developed. The computational cost can efficiently reduce under this three matrices multiplication pattern, shown as Fig.1 (b).

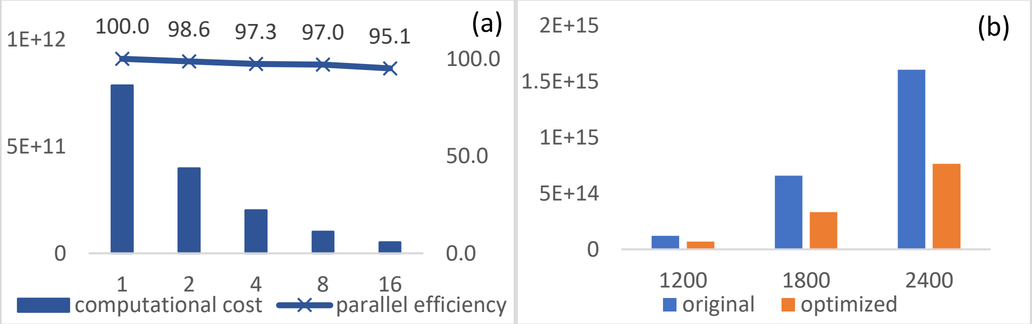

Figure 1. (a) Computational cost and parallel efficiency for tensor network parallelism. (b) Computational cost for original and optimized 3MM calculation at different bond dimension.

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Kylin 1.2: An Advanced Ab-initio Density Matrix Renormalization Group Program

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Kylin [1] is an ab-initio quantum chemistry program designed for efficient density matrix renormalization group (DMRG) and post-DMRG calculations. Recently, we further develop Kylin 1.2 version, where the DMRG codes are optimized and thus the calculation time is remarkably reduced. The major features of Kylin are listed in Table I.

Table I. Major features of Kylin.

Feature	Notes
RHF/UHF	DIIS/C^2-DIIS/EDIIS supported
MP2	
FCI/CASCI	Based on GUGA, ~14 active orbitals
DMRG	Mixed precision [2] supported, ~100 active orbitals
CASSCF/DMRG-SCF	Werner-Meyer-Knowles method implemented
UC-MRCI	
(DMRG-/sCI-)EC-MRCI	Spin-adapted [3], ~300 external orbitals
Geometry optimization	HF/CASSCF/DMRG-SCF level supported

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A Multi-reference Random Phase Approximation Theory

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Random phase approximation (RPA) has been widely used to compute the electron correlation energy for molecules and materials. However, conventional RPA typically breaks down with the presence of strong correlation, as it is based on a single determinant reference. To handle this problem, we formulated a multi-reference (MR) generalization of RPA for electron correlation energy by resumming a set of generalized ring diagrams, which are built on an interacting zeroth-order Hamiltonian containing strong correlation (e.g. Dyall's Hamiltonian). We also derived an MR second-order screened exchange (SOSEX) correction from a coupled-cluster perspective of the resulting MR-RPA to further include exchange effects. Numerical results demonstrate that MR-RPA/SOSEX resolves the failure of the conventional RPA/SOSEX for molecular dissociation. Our work bridges diagrammatic techniques in many-body physics and multi-reference perturbation theory in quantum chemistry, opening up new possibilities for computational studies of strongly correlated electrons via diagrammatic resummation.

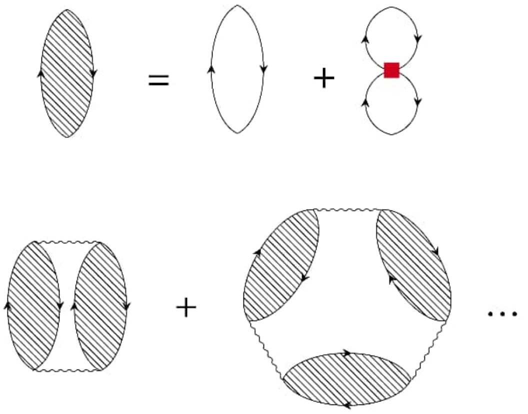

Figure 1. Generalized ring diagrams and resummation

Diffusion quantum Monte Carlo studies multi-reference systems

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The diffusion quantum Monte Carlo (DMC) method is crucial for solving the multi-body problem in quantum mechanics[1]. DMC offers precise calculations for single reference state systems using single determinant and Jastrow factor trial wave functions[3]. However, for multi-reference systems, employing CASCI and multi-determinant wave functions is essential for accurate results[4]. Utilizing untruncated CASCI wave functions in DMC calculations requires significant computational effort, usually necessitating truncation[5]. If the same truncation thresholds are used for both the reactants and the products in the reaction, there may be a large discrepancy between the dissociation reaction energies derived and the experimental values. The dissociation reaction energy results can be improved by lowering the determinant coefficient truncation threshold or extrapolating to a DMC energy result where the sum of the squares of the determinant coefficients is one. Besides, the size of the active space also has an effect on the calculation results, so we explored the extrapolated dissociation reaction energy results for different active spaces. For some multi-reference systems, it is difficult to obtain energy difference results that can be canceled out by systematic errors. We further use the adaptive variational active space (AVAS) method to select suitable orbitals to obtain CASSCF or CASCI wave functions for DMC calculations to get the extrapolated dissociation reaction energies.

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Exact analytic solutions of Schrödinger equations with non-separable variables: A case study of 1D quartic potential

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Traditional wavefunction methods based on basis-expansions typically express the wavefunction as a summation in Hilbert space, $\Psi = \sum_i c_i \Phi_i$. This form merely approximates or fits the wavefunction, failing to capture its analytic structure. We argue that a formally exact and practically useful analytic structure should be applicable over the entire space, reflect clear asymptotic behavior, and isolate easily approximable small quantities. We approach wavefunction from a novel perspective, transforming the Schrödinger equation into a Riccati equation through $\Psi = C\mathrm{e}^{\beta}$, solving for the derivative of β to obtain the wavefunction. We propose that the best representation of the wavefunction is an exact factorlization, consisting of a prefactor power function, an exponential decay term, and a modulator.[1-2] The modulator is a slowly varying, bounded function, which, for general Coulomb systems, can be represented as a convergent infinite analytic series over the entire space. We extended the new method to non-separable two- and three-electron problems, using a 1D quartic potential model as an example, deriving the analytic expression for the ground state wavefunction.[3] Similar to one-electron problems, the two- and three-electron wavefunctions exhibit clear analytic structures and distinct real-space asymptotic decay behavior.

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Formally Exact and Practically Useful Analytic Solution of Harmonium

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We provide a novel exact analytic solution of harmonium with arbitrary Coulomb interaction strength, for ground as well as all the excited states, using our recently developed method for solving Schrödinger equations. By comparing three formally exact analytic representations of the wave function including the one that utilizes bi-confluent Heun function, we find that the best and practically useful representation for the ground state is given by an exact factorized form involving a non-integer power pre-exponential factor, an exponentially decaying term and a modulator function. For excited states, additional factors are needed to account for the nodal information. We show that our method is far more efficient than basis-expansion-based methods in representing the wave function. With the exact wave functions, we have also analyzed the evolution trends of the electron density and natural occupation numbers with increasing interaction strength, which gives insight into the interesting physics in the strong correlation limit.

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Distinct Single-Electron Actinide−Actinide Bonding and Fullerene-Enhanced Magnetism in Two-Dimensional Diactinide Endohedral Metallofullerene Monolayers

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Recently, a two-dimensional quasi-hexagonal-phase fullerene (2D qHPC_{60}) monolayer has been experimentally synthesized.[1] We investigated the electronic structure and magnetism of 2D diactinide EMFs monolayers, referred to as $M_2@C_{60}$-2D (M_2 = U_2 or Th_2). Theoretical studies confirm the kinetic and thermodynamic stability of these constructed 2D monolayers, highlighting their significant potential for experimental synthesis. We reveal strong actinide–actinide bonding, with five one-electron-two-center (OETC) U–U bonds and two OETC Th–Th bonds formed inside fullerene. Further calculations show that the $U_2@C_{60}$-2D monolayer exhibits an antiferromagnetic (AFM) singlet ground state. In contrast, the $Th_2@C_{60}$-2D monolayer shows a ferromagnetic (FM) ground state. Our work extends the study of the unique bonding motifs and magnetism from isolated EMF to 2D EMF monolayers.

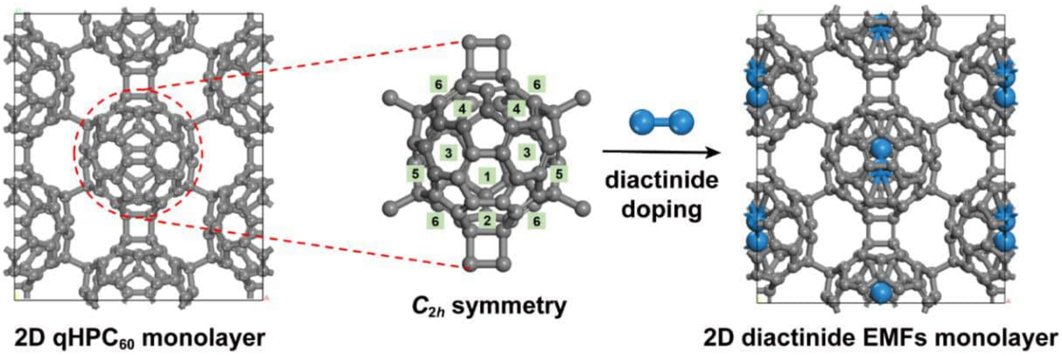

Figure 1. The construction of two-dimensional diactinide endohedral metallofullerene monolayers.

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Molecular Descriptors for High-Throughput Screening of Inverted Singlet−Triplet Gap Materials

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The new generation of proposed light-emitting molecules for organic light-emitting diodes (OLEDs) has raised considerable research interest due to its exceptional features—invert singlet-triplet (IST) gap violating Hund's multiplicity rule in the excited S_1 and T_1 states[1]. It is particularly challenging to discover new ones through virtual screening because the required wavefunction-based methods are expensive and unsuitable for high throughput calculations. Here, we propose a four-orbital model (FOM) considering both single and double excitation of electrons. Based on this model, two simple molecular descriptors (orbital difference $\Delta\varepsilon$ and exchange integral K) are developed to pre-screen candidate with IST features. Then the complex advanced methods are used to further screen the molecules, and finally a group of new IST cores are selected, and the state-of-the-art multireference method (ENVPT2) is used to verify that the singlet and triplet energy of these molecules has a reverse relationship. The discovery of these new IST cores provides a new perspective for the development of OLED light-emitting layer materials.

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Employing uncertainty-driven active learning strategies to construct full-dimensional intermolecular potential energy surfaces within spectroscopic accuracy

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Constructing reliable potential energy surfaces (PESs) is an important task for spectroscopic calculation. Normally, the number of potential points used for PES fitting will grow dramatically fast with the increasing of the dimension of systems, which makes it expensive or even unfeasible to calculate the fitting set by high-level electronic structure methods. This problem becomes important when we want to comprehensively study the monomer-flexibility effects of molecular complex systems since the intra-molecular vibrations will no longer be restricted and the dimension of intermolecular PES will increase a lot.

In this work, we employ uncertainty-driven active learning strategies to achieve efficient point samplings for MLRNet[1] and the permutationally invariant polynomial neural network[2]. This kind of sampling method has shown good performance for the PIP-NN to construct reactive PES samplings[3], and our results demonstrate that it is also reliable for the MLRNet and the PIP-NN to construct spectroscopically accurate PES. The model uncertainty is defined as the negative of the weighted square difference between two NN models trained with the same dataset but started with different initial NN parameters. The active learning would then search the maximum uncertainty points in a given configuration space. The initial set can be generated by quasi-random sampling, or by an optimization procedure based on one-dimensional Morse/Long-range (MLR) fitting in order to provide an initial estimation of the region of MLR parameter functions. For the 6-D H_2O-He system, 500 to 600 fitting points are enough to achieve a RMSE below 0.1 cm^{-1} for 38911 test points that energy below 0.0 cm^{-1}. The spectroscopic calculation results further support their accuracy.

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Learning Molecular Conformational Energies Using Semi-Local Density Fingerprints

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In this work, we introduce the **S**emi-**L**ocal **D**ensity **F**ingerprint (SLDF), a molecular descriptor that transforms the most energetically-relevant information in the electron density into feature vectors for machine learning (ML) the quantum mechanical properties of chemical systems. As a molecular descriptor for ML models, SLDFs offer a number of advantages, including (but not limited to): (1) a compact and fixed-size representation for each molecule, thereby enabling straightforward comparisons between different chemical species; (2) a feature vector that intrinsically accounts for molecular symmetry and is invariant to translations, rotations, and permutations; and (3) a unique atomic-species-independent representation of each molecule, with the potential for enhanced transferability across the periodic table. In a series of proof-of-principle tests, we demonstrate that SLDF-based ML models reduce density functional theory (DFT) conformational energy errors by 1-2 orders of magnitude, resulting in molecular conformational energies with errors <1 kJ/mol and some approaching spectroscopic accuracy (≈ 1 cm^{-1}). Greatly improved transferability across different chemical species is also demonstrated by testing SLDF-based ML models under three challenging learning strategies and illustrating its ability to correct the qualitatively-incorrect semi-local DFT description of the oxirene potential energy surface.

FIG. 1. Graphical illustration of the SLDF generation process starting from an input density $\rho(\boldsymbol{r})$. (a) Transformation of $\rho(\boldsymbol{r})$ into a continuous $\xi(u)$ function. (b) SLDF construction using B-splines. (c) A visual representation of the exchange-SLDF for four selected molecules. (d) Exchange-SLDF for four different conformations of the water molecule.

Development of a Compact Ansatz via Operator Commutativity Screening to Avoid Local Traps and Barren Plateaus

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Variational quantum eigensolver (VQE) provides a lucrative platform to determine molecular energetics on noisy intermediate scale quantum (NISQ) architecture. VQE relies on the construction of a wavefunction ansatz that ideally should be expressive yet sufficiently compact for NISQ realization. To address this, we come up with a robust ansatz construction protocol[1,2] that automatically adapts itself depending on the degree of correlation of the system through one and two parameter energy optimization, ordering and operator commutativity pre-screening. Furthermore, the construction can potentially be done in parallel quantum architecture. We have further compactified our dynamic ansatz by adaptively increasing the ansatz length at each step, investigating the effects of various numerical challenges, such as barren plateaus and numerous local minima. Our analysis indicates that the method COMPASS[1] with optimal block reordering, with its dynamic parameter inclusion, effectively avoids these local traps and barren plateaus by design. Further we have introduced a strategy for the inclusion generalized operators in projective quantum eigensolver (PQE) framework to reduce the quantum resource requirements.

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