In order to promote the development of frontier disciplines of surface physical chemistry, the State Key Laboratory of Physical Chemistry of Solid Surfaces has been organizing series Xiamen Workshop on Surface Chemistry since 1999. The workshops have been held every two years, with different themes selected each time. A total of ten workshops have been held so far. The purpose is to provide an important platform for international exchange and discussion on latest research results in the related fields, and to promote international exchange and cooperation of the Laboratory.

The 11th Xiamen workshop on surface chemistry will focus on excited-state electronic structure and dynamics theories of complex systems. The aims are to gather together scientists active in the development and application of theoretical methods to describe excited states as well as quantum dynamics of complex molecular systems to understand chemical quantum phenomena occurring in condensed and heterogeneous environments.

Organizing Committee of 2019 WSC

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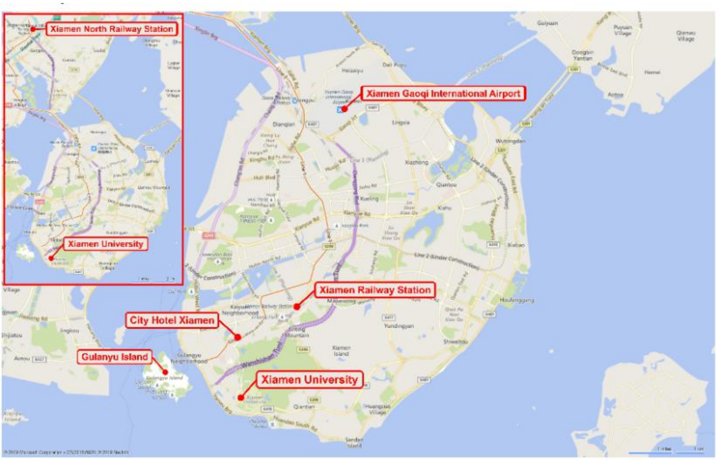
Venue:

All talks will be held in the Room 202, Lujiaxi Building.

The poster session will be in the lobby of Lujiaxi Building.

The Map of Xiamen:



The Map of Xiamen University:

Scientific Program

	12th Dec	13th Dec	14th Dec
8:45-9:00	**Opening Remarks**		
9:00-10:15	**Electronic structure**	**Electronic structure**	**Electronic structure & dynamics**
	Weitao Yang	Wenjian Liu	Yijing Yan
	John Herbert	Denis Jacquemin	Jochen Blumberger
	Shuhua Li	Yihan Shao	Oleg Prezhdo
10:15-10:40	Coffee break		
10:40-12:20	**Dynamics**	**Dynamics**	**Electronic structure & dynamics**
	Yoshitaka Tanimura	Oliver Kühn	Zhigang Shuai
	Jianshu Cao	Qiang Shi	Ganglong Cui
	Young Min Rhee	Maxim F. Gelin	Pavlo Dral
	Chaoyuan Zhu	Yuan-Chung Cheng	
12:20-14:00	Lunch & Posters		
14:00-15:15	**Electronic structure & dynamics**	**Electronic structure & dynamics**	Framed Discussions
	Xiaosong Li	Guanhua Chen	
	Aurélien de la Lande	Chao-Ping Hsu	
	ChiYung Yam	Jing Ma	
15:15-15:40	Coffee break		
15:40-17:20	**Electronic structure & dynamics**	**Dynamics**	
	Jiali Gao	Zhenggang Lan	
	Keli Han	Jian Liu	
	Hongxing Zhang	Guohua Tao	
	Yuchen Ma		

Dec. 12		
Session 1: Electronic structure Chair: Wei Wu		
08:45-09:00	Opening Remarks	
09:00-09:25	Weitao Yang (Duke University)	Electronic Excitation Energies from (N-2)-Electron Systems and (N-1)-Electron Systems
09:25-09:50	John Herbert (Ohio State University)	Spin-Flip TDDFT for Photochemistry
09:50-10:15	Shuhua Li (Nanjing University)	Local Excitation Approximation for Excited States of Large Systems
10:15-10:40	Group Photo & Coffee Break	

Session 2: Dynamics Chair: Zexing Cao		
10:40-11:05	Yoshitaka Tanimura (Kyoto University)	Modeling, Simulating, and Analyzing Nonadiabatic Dynamics: The Multi-State Quantum Fokker-Planck Approaches
11:05-11:30	Jianshu Cao (MIT)	Exciton Dynamics and Spectra of Organic Semiconductors
11:30-11:55	Young Min Rhee (Korea Advanced Institute of Science and Technology)	How Resonant Chromophore Vibrations Involve in Excitation Energy Transfers in Photosynthetic Complexes

11:55-12:20	Chaoyuan Zhu (National Chiao Tung University)	Functional and Basis Set Dependence for TDDFT Trajectory Surface Hopping Molecular Dynamics Simulation: Azobenzene Photoisomerization
12:20-14:00	Lunch & Poster Presentation (Lobby, Lujiaxi Building)	
Session 3: Electronic Structure & Dynamics Chair: Deyin Wu		
14:00-14:25	Xiaosong Li (University of Washington)	Toward the Evaluation of Intersystem Crossing Rates with Variational Relativistic Methods
14:25-14:50	Aurélien de la Lande (Université Paris-Sud)	Toward First Principles Simulations of Biological Matter under Ionizing Radiations

14:50-15:15	ChiYung Yam (Beijing Computational Science Research Center)	Theoretical Investigation of Current-Induced Light Emission in Scanning Tunneling Microscopy Molecular Junctions
15:15-15:40	Coffee Break	
Session 4: Electronic Structure & Dynamics Chair: Binju Wang		
15:40-16:05	Jiali Gao (Peking University Shenzhen Graduate School)	Allosteric Regulation of Light-Harvesting and Quenching
16:05-16:30	Keli Han	Charge-Carrier Dynamics of Lead-Free Halide Perovskite

	(Dalian Institute of Chemical Physics)	Nanocrystals
16:30-16:55	Hongxing Zhang (Jilin University)	Quantum Dynamic Investigation of Interfacial Electron Transfer
16:55-17:20	Yuchen Ma (Shandong University)	Energy Transfer from Carotenoids to Chlorophylls in Photosynthesis: The Role of a New Dark Excited State
18:00-20:30	Banquet (Lin Wutong Building)	

Dec. 13		
Session 5: Electronic structure Chair: WanZhen Liang		
09:00-09:25	Wenjian Liu (Shandong University)	Iterative Configuration Interaction with Selection
09:25-09:50	Denis Jacquemin (University of Nantes)	The BSE/GW Approach: a New Tool for Excited State Modelling in Chemistry
09:50-10:15	Yihan Shao (University of Oklahoma)	New Computational Tools for Analyzing Substituent Effects and Energy Distribution
10:15-10:40	Coffee Break	

Session 6: Dynamics Chair: Peifeng Su		
10:40-11:05	Oliver Kühn (University of Rostock)	Unraveling the Elementary Steps of Photosensitizer Dynamics Using Methods Across the Spectrum from IR to X-ray
11:05-11:30	Qiang Shi (Institute of Chemistry, CAS)	Theoretical Study of Ultrafast Dynamics and Spectroscopy in Natural and Artificial Molecular Systems
11:30-11:55	Maxim F. Gelin (Hangzhou Dianzi University)	Thermal Schrödinger Equation: Efficient Tool for Simulation of Many-Body Quantum Dynamics at Finite Temperature

11:55-12:20	Yuan-Chung Cheng (National Taiwan University)	Two-Dimensional Electronic Spectroscopy of Nonadiabatic Dynamics
12:20-14:00	Lunch & Poster Presentation (Lobby, Lujiaxi Building)	
Session 7: Electronic Structure & Dynamics Chair: Zhenhua Chen		
14:00-14:25	Guanhua Chen (University of Hong Kong)	Coherent Real-Space Charge Transport Across a Donor−Acceptor Interface Mediated by Vibronic Couplings
14:25-14:50	Chao-Ping Hsu (Institute of Chemistry Academia Sinica)	Excitation Energies from Thermally-Assisted-Occupation Density Functional Theory

14:50-15:15	Jing Ma (NanJing University)	Theoretical Study on Merger of Photoredox and Transition Metal Catalysis
15:15-15:40	Coffee Break	
Session 8: Electronic Structure & Dynamics Chair: Jun Zhu		
15:40-16:05	Zhenggang Lan (South China Normal University)	Nonadiabatic Dynamics and Machine Learning
16:05-16:30	Jian Liu (Peking University)	A New Perspective for Nonadiabatic Statistics and Dynamics
16:30-16:55	Guohua Tao	Topology of Quantum Coherence Network in Singlet

	(Peking Univ. Shenzhen Graduate School)	Fission
17:30-20:30	Dinner (Shuyou Restaurant in Bailuzhou)	

Dec. 14		
Session 9: Electronic Structure & Dynamics Chair: Pavlo Dral		
09:00-09:25	Yijing Yan (University of Science and Technology of China)	Onsets of Dissipaton Equation of Motion Theory
09:25-09:50	Jochen Blumberger (University College London)	Quantum Localization and Delocalization of Charge Carriers in Organic Semiconducting Crystals
09:50-10:15	Oleg Prezhdo (University of Southern California)	Excited State Dynamics in Hybrid Materials for Solar Energy Harvesting

10:15-10:40	Coffee Break	
Session 10: Electronic Structure & Dynamics Chair: Yi Zhao		
10:40-11:05	Zhigang Shuai (Tsinghua University)	Finite Temperature Time Dependent Density Matrix Renormalization Group for Exciton-Phonon Model
11:05-11:30	Ganglong Cui (Beijing Normal University)	Integrating Machine Learning and Multi-Layer Energy-based Fragment Method for Excited States and Nonadiabatic Dynamics
11:30-11:55	Pavlo Dral (Xiamen University)	Machine Learning and Semiempirical Methods for Nonadiabatic Dynamics
12:00-14:00	Lunch	

Electronic Excitation Energies from (N-2)-Electron Systems and (N-1)-Electron Systems

Weitao Yang
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School of Chemistry and Environment, South China Normal University

Electronic excitation energies are usually obtained computationally from the dynamic density fluctuations of the system, as in time-dependent density functional theory (TDDFT) and the Bethe-Salpeter many-body Green’s function approach. Double, Rydberg, and charge transfer (CT) excitations and conical intersections have been great challenges for TDDFT. To overcome such challenges, we have developed effective methods using reference systems of different number of electrons. Starting from an (N-2)-electron reference, we investigated excitations for the N-electron system through the pairing matrix fluctuations, which contains information on two-electron addition/removal processes. We adopt the particle-particle random phase approximation (pp-RPA) and the particle-particle Tamm-Dancoff approximation (pp-TDA) to approximate the pairing matrix fluctuation and then determine excitation energies by the differences of two-electron addition/removal energies. This approach captures all types of interesting excitations: single and double excitations, Rydberg excitations and CT excitations. With the active space approach, the pp-RPA and the pp-TDA have a computational cost of (K^4) . Starting from an (N-1)-electron reference, we developed the quasiparticle energy DFT (QE-DFT) approach that captures excitation energies of the N-electron systems from the virtual orbitals energies of the (N - 1)-electron system in the ground state density functional theory calculations. This is based on the capability of approximating quasiparticle energies from the ground state DFT orbital energies with the recently developed localized orbital scaling correction (LOSC). LOSC was developed to achieve a universal elimination of the delocalization error in DFT. Comparison of experimental quasiparticle energies for many finite systems with calculations from the GW Green function approach and LOSC shows that LOSC orbital energies achieve slightly better accuracy than the GW calculations with little dependence on the semilocal DFA. QE-DFT shows good performance for valence excitations with commonly used DFAs with or without LOSC, for Rydberg states only with the use of LOSC-DFA, and the accurate description of conical interactions. QE-DFT is a new and simplest pathway to describing excited states.

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10. Yang, Y., Shen, L., Zhang, D. & Yang, W. T. Conical Intersections from Particle-Particle Random Phase and Tamm-Dancoff Approximations. *Journal of Physical Chemistry Letters* **7**, 2407–2411 (2016).
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Spin-Flip TDDFT for Photochemistry

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Although time-dependent density functional theory (TDDFT) is ubiquitous for calculation of ground-state absorption spectroscopy, and has been used in surface-hopping-type simulations of nonadiabatic excited-state dynamics, certain fundamentalissues preclude its more widespread adoption for photochemical simulations. One of these is an incorrect topological description of conical intersections that involve the ground state, where TDDFT predicts branching spaces that are one-dimensional ratherthan two-dimensional. The topology problem can be rectified through the use of a spin-flip variant of TDDFT, for which we have derived and implemented analytic derivative coupling vectors for efficient location and optimization of photochemical seams. Forexcited-state dynamics, however, the use of spin-flip TDDFT is hampered by spin contamination problems. This problem can be avoided using a “spin complete” version of the theory that adds the minimal number of determinants necessary to obtain proper spineigenfunctions. This “spin-adapted spin-flip” version of TDDFT retains the same formal computational scaling as conventional TDDFT but affords a proper description of conical intersections, and all states have well-defined spin multiplicities.

Local excitation approximation for excited states of large systems

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In this talk, I will present our recent advances in developing electronic structure methods for excited states of large systems. We have developed two types of excited state methods for large systems. The first approach is called as local excitation approximation (LEA) based time-dependent density functional theory (TDDFT) or time-dependent Hartree-Fock (TDHF) [1]. The main idea of the LEA scheme is that only local electron excitations within a certain active region (called as chromophore) are treated to obtain the excitation energies for locally excited electronic states. We have proposed an efficient localization procedure to obtain regional localized molecular orbitals localized on the chromophore subunit. For acetone in aqueous solution, LEA-TDDFT calculations on 600 acetone-water configurations suggest that the calculated blueshift in the $n \rightarrow \pi^*$ vertical electronic excitation energy is in good agreement with the available experimental blue shift. Another approach is the generalized energy-based fragmentation (GEBF) approach for localized excited states [2]. In this approach, the excited-state energy of a large system could be expressed as the combination of the excited-state energies of "active subsystems", which contains the chromophore center, and the ground-state energies of "inactive subsystems". The GEBF approach has been implemented at the levels of TDDFT and approximate coupled cluster singles and doubles (CC2) method. Our results show that GEBF-TDDFT can reproduce the TDDFT excitation energies and solvatochromic shifts for large systems and GEBF-CC2 could be used to validate GEBF-TDDFT result (with different functionals). The GEBF-TDDFT method is found to be able to provide satisfactory descriptions on the experimental solvatochromic shifts for the $n \rightarrow \pi^*$ transitions of acetone in various solutions, and the lowest $\pi \rightarrow \pi^*$ transitions of pyridine in aqueous solution.

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Modeling, simulating, and analyzing nonadiabatic dynamics:The multi-state quantum Fokker-Planck approaches

Yoshitaka Tanimura
Kyoto University, Department of Chemistry, Kyoto, Japan.

Open quantum system refers to a primary quantum system that is embedded in a heat bath represented by an infinite number of sub quantum systems. The key feature of this system is that it describes irreversible dynamics refers to open quantum dynamics through which the primary system evolves toward the thermal equilibrium state at finite temperature. Quantum coherence and its dephasing or relaxation by coupling to an environment plays an important role in nonadiabatic transition and photoexcitation as well as ultrafast nonlinear spectroscopies. By generalizing the quantum hierarchal equations (QHE)[1,2] to a multi-electric states, we can investigate photoisomerization process described by anharmonic potential surfaces with multi-electric state numerically rigorously.[3-7] We developed a computer code that can treat the multi-state system in a phase space with any profile of laser pulse and any strength of non-adiabatic coupling under non-perturbative and non-Markovian system-bath interactions.[4,5] The approach applies to the calculation of linear and nonlinear spectra for a system described by the multistate 1D [3-6] and 2D [7] potential surfaces. We computed nuclear wave packets in Wigner representation and their monitoring by linear absorption, transient absorption, and multi-dimensional electric spectra for various heat-bath parameters to explore photoisomerization dynamics by means of spectroscopic measurements. The movement of excitation and ground state wave packets and their coherence involved in the process were observed as the profiles of positive and negative peaks of 2DEVS spectrum.

Our ongoing research for modeling anharmonic Brownian model system on the basis of MD trajectories using machine learning technique will be also explained. [8]

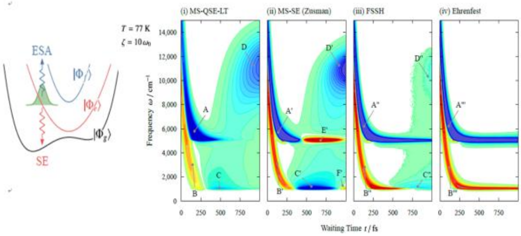

Fig.1 Transient absorption spectra of a three-state system (left figure) for an overdamped case obtained from the (i) Low-Temp. Multi-State quantum Smoluchowski Eq. (LT-MS-QSE) (ii) multi-state classical Smoluchowski Eq. (MS-SE or Zusman Eq.), (iii) fewest switch surface hopping (FSSH) methods, and (iv) Ehrenfest methods, respectively. (Ref. [5])

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Exciton Dynamics and Spectra of Organic Semiconductors

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(I) Calculations of coherent quantum transport in disordered organic systems reveal an optimal diffusion constant at an intermediate level of noise and temperature and predict charge mobility close to experimental values. [1] Further, we have explored the dependence on the dimensionality and shape and demonstrated the universal scaling of the 1D-2D transition in the diffusion of nanotubes [2]. Though transport is suppressed by disorder, trapping or dissociation can be enhanced by disorder. [3]
(II) Spectroscopic measurements of nanotubes and 2D systems allow us to classify the structure of dipolar lattices beyond the simple rule of H and J aggregates. [4]
Further, we have studied the scaling laws in the spectral shift, splitting, and width, and related them to the structure of molecular aggregates. [4,5]

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hopping and band-like transport” Lee, Moix, Cao, JCP 142, 164103 (2015)
(2) “Quantum diffusion on molecular tubes: Universal scaling of the 1D to 2D transition”. Chuang,
Lee, Moix, Knoester, and Cao, Phys. Rev. Lett. 116, 196803 (2016)
(3) “Generic mechanism of optimal energy transfer efficiency: A scaling theory of the mean first
passage time in exciton systems” Wu, Silbey, Cao, Phys. Rev. Lett 110 (20), 200402 (2013)
(4) “Generalized Kasha's Scheme for Classifying Two-Dimensional Excitonic Molecular Aggregates:
Temperature Dependent Absorption Peak Frequency Shift” Chuang, Bennett, Caram, Aspuru
Guzik, Bawendi, J Cao, accepted by CHEM. (2019)
(5) “Construction of multichromophoric spectra from monomer data: Applications to resonant
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How resonant chromophore vibrations involve in excitation energy transfers in photosynthetic complexes

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In photosynthetic complexes, the exciton-phonon coupling works importantly toward governing the energy transport. Indeed, it is now widely discussed that the chromophore units composing the complexes have certain harmony and balance in their electronic and vibrational structures. Especially, when a chromophore vibration energy is close to be in resonance with the electronic excitation energy, severe mixing takes place to control the energy transfer. Therefore, elucidating how these two aspects combine together will be beneficial toward artificially designing new functional systems. Theoretical approaches have been proven to be quite useful in this regard, but they have been limited by their reliability in treating vibrations especially when one seeks to explore atomistic details. Basically, adopting quantum chemical tools is unavoidable, but doing so costs too much especially toward treating dynamic aspects over time. In this talk, we will discuss what information has been and can further be attained with the recently constructed atom-specific potential models of two representative complexes, FMO and LH2, based on interpolation mechanics / molecular mechanics (IM/MM) technique in combination with the density functional theory calculations. In addition, based on a simplified model, we will next show that the resonant behavior in the vibronic coupling toward energy transfer bears strong classical nature. Even still, we will show that the details of electronic-vibrational energy exchanges are beyond the description of classical mechanics, although classical treatment tends to be all right in reasonably disordered situations. How these observations combine together toward employing all-atom style descriptions will be discussed as a concluding remark of the talk.

Functional and basis set dependence for TDDFT trajectory surface hopping molecular dynamics simulation: azobenzene photoisomerization

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Within three functionals TD-(B3LYP, BHandHLYP and CAM-B3LYP) in combination with 4 basis sets (3-21g, 6-31g, 6-31g(d), and cc-pvdz), global switching trajectory surface hopping molecular dynamics have been performed for cis-to-trans azobenzene photoisomerization up to the S1(nπ*) excitation. Although all the combinations show artificial double-cone structure of conical intersection between ground and first excited states, simulated quantum yields and lifetimes are in good agreement with one another; 0.6 (±5%) and 40.5fs (±10%) by TD-B3LYP, 0.5 (±10%) and 35.5fs (±4%) by TD-BHandHLYP, and 0.44 (±9%) and 35.2fs (±10%) by TD-CAM-B3LYP. By analyzing distributions of excited-state population decays, hopping spots, and typical trajectories with performance of 12 functional/basis-set combinations, it has been concluded that functional dependence for given basis set is slightly more sensitive than basis set dependence for given functional. The present global switching on-the-fly TDDFT trajectory surface hopping simulation can provide practical benchmark guidelines for conical intersection driven excited-state molecular dynamics simulation involving in large complex system within ordinary TDDFT framework.

Toward the Evaluation of Intersystem Crossing Rates with Variational Relativistic Methods

Xiaosong Li
University of Washington

The change of electronic state from one spin multiplicity to another, known as intersystem crossing, occurs in molecules via the relativistic phenomenon of spin-orbit coupling. Current means of estimating intersystem crossing rates rely on the perturbative evaluation of spin-orbit coupling effects. This perturbative approach, valid in lighter atoms where spin-orbit coupling is weaker, is expected to break down for heavier elements where relativistic effects become dominant. Methods which incorporate spin-orbit effects variationally, such as the exact-two-component (X2C) method, will be necessary to treat this strong-coupling regime. We present a novel procedure which produces a diabatic basis of spin-pure electronic states coupled by spin-orbit terms, generated from fully variational relativistic calculations. This method is implemented within X2C using time-dependent density-functional theory, and is compared to results from a perturbative relativistic study in the weak spin-orbit coupling regime. Additional calculations on strongly spin-orbit-coupled unramium complex and di-Pt molecular system further illustrate the strengths of this method. This procedure will be valuable in the estimation of intersystem crossing rates within strongly spin-coupled species.

Toward First Principles Simulations of Biological Matter under Ionizing Radiations

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The transient collision (10^{-17} s) of high-energy-transfer particles with biological matter results in ionization or excitation of its constituent molecules. Huge amounts of energy are deposited locally, typically several tens of eV. These early physical events produce a myriad of reactive radical species that are at the source of cascades of chemical processes spanning several spatial and temporal scales. The physical chemistry of these ultrafast processes are not well understood at the present time.

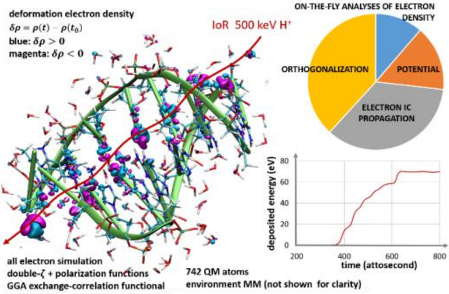

Figure: Irradiation of 10-base DNA double strand by a 500 keV proton particle. The left panel depicts isosurfaces of the deformation density just after irradiation. On the right panel a graph shows the increase of deposited energy as a function time (bottom) and the main computational tasks involved in he simulation (top)

During this seminar I will introduce an original set of methodologies that we have devised to investigate these phenomena from first principles [1,2]. These are based on Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) and Ehrenfest Molecular Dynamics (MD) simulations. A hybrid scheme coupling these approaches to polarizable force fields have been devised to simulate large biological systems. This implementation includes explicit time propagation of the electric fields mediating interaction between the quantum and classical parts of the system[3].

Theses methodologies have been implemented in deMon2k. Our approach allows simulations of collisions of molecules with HET, and subsequent ionization, ultrafast charge migration, energy relaxation/dissipation on the attosecond time scale (cf. Figure). Ehrenfest MD

further gives access to non-adiabatic chemical reactivity taking place in the first femtoseconds after irradiation.
I will introduce the methodologies and applications to various questions of current high interest in radiation chemistry.

Acknowledgments: We thank the French ANR (ANR-15-CE29-0011-01) and CNRS (projet Emergence@INC, 2018).

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[4] Non-Adiabatic Molecular Dynamics simulations in the framework of Auxiliary Time-Dependent Density Functional Theory. A. Alvarez-Ibarra, K. Hasnaoui,.., A. de la Lande. In preparation.

Theoretical investigation of current-induced light emission in scanning tunneling microscopy molecular junctions

Xiaoyan Wu, Rulin Wang, Yu Zhang,
Bowen Song and ChiYung Yam
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Tunneling electron-induced light emission in scanning tunneling microscopy (STM) has recently been explored as a novel light source with tuneable properties. We employed density-functional tight-binding (DFTB) to study the STM-induced luminescence of a single-molecule emitter and propose a way to control the emission frequency of the STM molecular junction by precisely controlling the charge injection at different molecular positions. The luminescence is found to be directly related to the spatial distribution of the molecular states and thus depends sensitively on the tip position. Via careful refinement of the chemical structures, devices with desirable frequencies at different parts of the emitting unit can be designed. Our proposal has profound implications for applications in nanoscale optoelectronics and future hybrid electronic-photonic circuits.

Allosteric Regulation of Light-Harvesting and Quenching

Yingjie Wang, Hao Li, Yuxian Weng，and Jiali Gao
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2Department of Chemistry, University of Minnesota, Minneapolis, MN, USA
3Physics Institute, Chinese Academy of Sciences, Beijing, China

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 an investigation combining molecular dynamics simulation and temperature-jump time-resolved IR spectroscopy to understand the mechanism of energy dissipation in LHCII. An allosteric regulation of the global protein conformational changes induced by local conformational transitions will be discussed. The dynamic motions induce close contacts between the associated chromophores to facilitate fluorescence quenching. In addition, I will discuss a multistate density functional theory designed to model photochemical and charge transfer processes.

Charge-Carrier Dynamics of Lead-Free Halide Perovskite Nanocrystals

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Lead halide perovskite nanocrystals (NCs) have been widely studied for application in optoelectronic devices due to their excellent optical properties and low-cost synthesis. However, the toxicity of lead and the poor stability of the NCs hindered their practical applications. Sn^{2+} based perovskite with low toxicity was firstly developed, however, the Sn^{2+} based perovskite NCs are unstable in air and oxidize easily. Recently, air-stable lead-free perovskite NCs have been developed and received increasing attention. Unfortunately, the optical and optoelectronic properties of these lead-free halide perovskite NCs are generally far worse than those of lead-perovskite NCs.

In 2017, we reported the charge-carrier dynamics of $Cs_3Bi_2X_9$ (X: Cl, Br, I) NCs. The $Cs_3Bi_2Br_9$ NCs exhibited clear exciton trapping processes with time scales in the range of 2-20 ps. The fast trapping processes could be passivated via the use of surfactants (such as oleic acid) and the PLQE increased over 20 fold (from 0.2% to 4.5%). The low PLQE may be due to the reduced dimensionality of $Cs_3Bi_2Br_9$ (2D) compared with the 3D cubic perovskite structure of $CsPbBr_3$. We next reported double perovskite $Cs_2AgSb_{1-y}Bi_yX_6$ (X: Br, Cl; $0 \le y \le 1$) NCs, which exhibited a similar 3D cubic perovskite structure to the lead-perovskite NCs. The charge-carrier dynamics indicated that the sub-bandgap exciton trapping processes were dominated by ultrafast (~1-2 ps) intrinsic self-trapping and trapping at surface defects (~50-100 ps).While trapping at surface defects can be passivated using surfactants (oleic acid), the self-trapping processes is due to the giant carrier-phonon coupling effect. By designing direct bandgap double perovskite NCs to tune the sub-bandgap trapping processes, bright dual-color emission was achieved. Furthermore, the violet PLQE could be improved to 36.6%, which is comparable to thatin lead halide perovskite NCs.We hope this Account will deepen the understanding of the charge-carrier dynamics in lead-free perovskite NCs and guide the design of high performance lead-free perovskites.

Quantum Dynamic Investigation of Interfacial Electron Transfer

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Energy Transfer from Carotenoids to Chlorophylls in Photosynthesis:

The Role of a New Dark Excited State

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Traditionally, only two singlet excited states of carotenoid (S_1 and S_2 in Fig.1a) were considered to take part in the energy transfer from carotenoids to chlorophylls in photosynthetic systems. Ever since Cerullo *et al*. reported their discovery of an intermediate singlet state (named S_x by them) between S_1 and S_2, which they suggested that may play some role in the energy transfer in photosynthesis [1], the character and the origin of S_x have aroused great attention and widely discussion. Recent two-dimensional electronic spectroscopy performed by Ostroumov *et al*. further demonstrates clearly the decay of S_2 to S_x and the energy transfer from S_x to chlorophylls [2]. According to the previous theory [3], S_x has been generally attributed to the state $1B_u^-$ (Fig.1b). However, this assignment is highly controversial due to the contradiction between properties of S_x measured experimentally and the behavior of $1B_u^-$ determined from both experiments and theory. Based on our calculations on excited-state dynamics and energy transfer by the many-body Green's function theory [4, 5], which includes the GW method and the Bethe-Salpeter equation, we suggest that S_x might be a new dark state with the A_g^+ symmetry (S_y in Fig.1c) [6]. Our calculated energy transfer efficiency between carotenoids and chlorophylls agrees with the experiment as well.

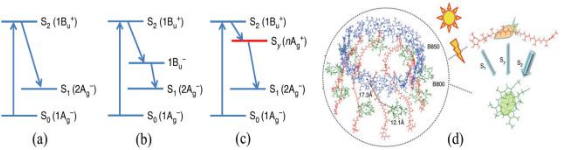

Figure 1: (a), (b) and (c): Different excited-state energy level models of carotenoids. (d): Structure of Rhodopseudomonas acidophila

Keywords: Carotenoid, Dark State, Photosynthesis, Energy Transfer, Many-Body Green's Function Theory

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Iterative Configuration Interaction with Selection

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Keywords: strong correlation; static-dynamic-static; SDSPT2; iCI; iVI; tabulated orbital-configuration based unitary group approach

Abstract: According to when the static and dynamic components of electron correlation are treated, the available wave function-based correlation methods can be classified into three families, viz., "static-then-dynamic", "dynamic-then-static", and "static-dynamic-static (SDS)" [1]. Herewith we report a *restricted* SDS framework [2], which employs *the same number* (Np; the number of target states) of primary, secondary and external states for describing the static, dynamic, and again static components of correlation. That is, the secular equation to be diagonalized is of dimension 3Np, irrespective of the numbers of correlated electrons and orbitals. Even the lowest-order realizations of this seemingly *restricted* SDS framework, i.e., SDSPT2 and SDSCI, are already very accurate for classic test problems of variable degeneracies [2,3], whereas a high-order realization, i.e., iCI (iterative Configuration Interaction), can converge monotonically and quickly to full CI from above, even when a rather poor reference is taken as the start [1]. Interestingly, the micro-iteration of iCI can be reformulated as an iterative Vector Interaction (iVI) method for exterior or interior roots of general large matrices[4,5]. In this lecture, we will introduce a tabulated orbital-configuration based unitary group approach (TOC-UGA) for the selection of important configurations in iCI, so as to make the latter as efficient as possible[6].

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The BSE/GW approach: a new tool for excited state modelling in chemistry

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Time-Dependent Density Functional Theory (TD-DFT) is the most widely used method to model electronically excited-states [1]. However, as its wavefunction alternatives, it suffers from a specific limitations. As a consequence, other methods able to reproduce excited-state properties at a moderate computational cost are always welcome, e.g., coupled-cluster (CC) or complete active space (CAS) methods have constituted chemists' workhorses for years. Among alternative approaches, the Bethe-Salpeter (BSE) scheme, an extension of the ground-state *GW* method, offers an appealing alternative to TD-DFT, as it maintains the same scaling with system size [2]. In this talk, the performances of BSE/*GW* for excitations energies of molecules will be presented, considering vertical transitions [3], 0-0 energies [4] and oscillator strengths [5]. It will be shown that a partial self-consistent scheme at the *GW* level leads to a significantly reduced dependency on the starting DFT functional compared to both TD-DFT and BSE/G_0W_0 [3,6], as well as an accuracy similar to the one of reference wavefunction approaches for singlet [6] but not for triplet [7] states. Finally, applications on large systems [8] as well as inclusion of solvent effects [9] will be discussed.

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New Computational Tools for Analyzing Substituent Effects and Energy Distribution

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In this talk, we will introduce two new computational chemistry tools. Firstly, we present an orbitals-interaction-based protocol (*Chem. Sci.* 9, 8598, 2018) to analyze the substituent effect on a fluorophore. Specifically, it shows how the fluorophore HOMO and LUMO interact with substituent orbitals to modulate the HOMO-LUMO gap and absorption/emission wavelengths. The utilization of this tool will be demonstrated using the oxyluciferin anion (firefly bioluminescence emitter) as an example.

Secondly, we will describe a scheme to compute the energy density of a Kohn-Sham DFT or TDDFT state on a real-space grid. This will allow us to analyze the real-space distribution of the energy difference arising from employing different sets of Kohn-Sham orbitals or from electronic excitations with LR-TDDFT. Such an energy distribution analysis will be showcased using the Ag_4-N_2 model complex.

Unraveling the Elementary Steps of Photosensitizer Dynamics Using Methods Across the Spectrum from IR to X-ray

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Transition metal complexes play an essential role as photosensitizers, photoemitters, and dyes. The theoretical description of mechanistic details of the associated processes are complicated due to (i) the nontrivial electronic structure with system sizes calling for density functional theory, which is challenged by correlation effects and charge transfer transitions, (ii) a pronounced spin-orbit coupling giving rise to spin forbidden mixing up to the point where a classification in terms of spin-free states ceases to make sense, and (iii) the practical use of photosensitizers as part of complex reaction schemes involving multiple reactants and products. All together these points are shaping the landscape of multidimensional nonadiabatic functional dynamics.

During the last years, we have applied electronic structure and theoretical spectroscopy methods to characterize the elementary steps of an exemplary hydrogen-generating photocatalytic cycle employing on an Ir-photosensitizer and a Fe-based water reduction catalyst. Our efforts comprised the electronic excitation and charge separation, the reduction of the photosensitizer as well as the electron transfer to the Fe-based catalyst. This talk will give an overview and address methodological challenges.

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Theoretical study of ultrafast dynamics and spectroscopy in natural and artificial molecular systems

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I will present some recent progresses in our group in simulation ultrafast dynamics and spectroscopy in condensed phase molecular systems. (1) **Simulation of two-color 2D spectra and excitation energy transfer dynamics in photosynthetic light-harvesting systems**. To include the effect of finite pulse width, we combine the hierarchical equations of motion method and the equation-of-motion phase-matching approach to obtain the two-dimensional electronic spectra (2DES). The 2DES of the light-harvesting complex II (LHCII) at room temperature are then simulated. The energy transfer pathways and time scales revealed from the 2DES agree with the recent experimental studies. We also propose a new way to identify signals of bottleneck states by investigating the diagonal peaks of the 2DES. (2) **Real time simulation of charge separation process at the donor/acceptor interface in organic photovoltaic (OPV) devices.** Charge separation dynamics with multiple timescales are indentified, including an ultrafast component within hundreds of femtoseconds, an intermediate component related to the relaxation of the hot charge transfer (CT) state, and a slow component on the timescale of tens of picoseconds from the thermally equilibrated CT state. Effects of hot exciton dissociation, as well as its dependence on the energy offset between the Frenkel exciton and the CT state are also analyzed. (3) Non-pertubative memory kernels and generating functions to study the charge transfer dynamics. By using the hierarchical equation of motion (HEOM) and extended HEOM methods, we present a new approach to calculate the exact time non-local and time-local memory kernels and their high order perturbative expansions. The new approach is applied to the spin-boson model with different sets of parameters, a model charge transport in organic molecular crystals.

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Thermal Schrödinger Equation: Efficient Tool for Simulation of Many-Body Quantum Dynamics at Finite Temperature

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I will give a brief overview of a recently developed wave-function-based method for the simulation of quantum dynamics of systems with many degrees of freedom at finite temperature. The method is inspired by the ideas of Thermo Field Dynamics (TFD). As TFD, the method is based on the doubling of the system's degrees of freedom and thermal Bogoliubov transformation. As distinct from TFD, the method implements the doubling of thermalized degrees of freedom only, and relies upon the explicitly constructed generalized thermal Bogoliubov transformation, which is not restricted to fermionic and bosonic degrees of freedom. The solution of TFD dynamic equations is based on the Tensor Trains (Matrix Product States) propagation technique. The methodology is illustrated by the simulation of the exciton dynamics in the Fenna-Mathews-Olsen complex using a realistic structured spectral density to model the electron-phonon interaction. The results of the simulations highlight the effect of specific vibrational modes on the exciton dynamics and energy transfer process, as well as call for careful modeling of electron-phonon couplings.

Two-Dimensional Electronic Spectroscopy of Nonadiabatic Dynamics

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Nonadiabatic transitions play crucial roles in photophysics and photochemistry, yet unambiguous determinations of the detailed dynamics remain a challenging task. Recently, time-resolved ultrafast spectroscopic techniques have contributed to many advances in probing nonadiabatic dynamics, in particular, two-dimensional electronic spectroscopy (2DES) provides a decisive probe for elucidating the detailed coupled electronic-vibrational dynamics. Nevertheless, because of the complexity of 2DES signals, theoretical simulations are required to develop understanding of the underlying processes. We have developed a quantum Langevin equation approach that enables calculations of 2DES signals for molecular systems from direct simulations of the light-driven, dissipative nonadiabatic wavepacket dynamics, allowing us to predict various 2DES spectra for nonadiabatic dynamics in condensed-phase molecular systems. This method has been applied to investigate 2DES of systems with nonadiabatic transitions through conical intersections. Furthermore, we have studied new experimental setup that could provide information not available in conventional 2DES experiments, and examples on applications of the proposed methods to search for spectroscopic signatures of conical intersections in organic molecules will be demonstrated. Our findings show that the theoretical simulation method is not only a powerful tool for the interpretations of experimental 2DES data but also an effective means for expanding the frontiers of ultrafast nonlinear spectroscopy.

Coherent Real-Space Charge Transport Across a Donor−Acceptor Interface Mediated by Vibronic Couplingshsu

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There is growing experimental and theoretical evidence that vibronic couplings, couplings between electronic and nuclear degrees of freedom, play a fundamental role in ultrafast excited-state dynamics in organic donor−acceptor hybrids. Whereas vibronic coupling has been shown to support charge separation at donor−acceptor interfaces, so far, little is known about its role in the real-space transport of charges in such systems. Here we theoretically study charge transport in thiophene:fullerene stacks using time-dependent density func- tional tight-binding theory combined with Ehrenfest molecular dynamics for open systems. Our results reveal coherent oscillations of the charge density between neighboring donor sites, persisting for ∼200 fs and promoting charge transport within the polymer stacks. At the donor−acceptor interface, vibronic wave packets are launched, propagating coherently over distances of more than 3 nm into the acceptor region. This supports previous experimental observations of long-range ballistic charge-carrier motion in organic photovoltaic systems and highlights the importance of vibronic coupling engineering as a concept for tailoring the functionality of hybrid organic devices.

Excitation Energies from Thermally-Assisted-Occupation Density Functional Theory

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The linear-response time-dependent density functional theory (LR-TDDFT) has been broadly used to investigate the excited-state properties of various molecular systems. However, current LR-TDDFT methods heavily rely upon outcomes from the corresponding ground-state density functional theory (DFT) calculations which may be prone to errors due to the lack of proper treatment in the non-dynamical correlation effects. Recently, thermally-assisted-occupation density functional theory (TAO-DFT) [J.-D. Chai, J. Chem. Phys. 136, 154104 (2012)], a DFT with fractional orbital occupations, was proposed, explicitly incorporating the non-dynamical correlation effects in the ground-state calculations with low computational complexity. In this work, we develop TDTAO-DFT, which is a time-dependent linear-response theory of excited states within the framework of TAO-DFT, to study the excited states of H_2. The correct feature of the first triplet excited state including the non-imaginary excitation energies, as well as zero singlet-triplet gap in the dissociation limit, are correctly predicted by TDTAO-DFT. In addition, the overall excited-state potential energy surfaces obtained from TDTAO-DFT also have excellent agreement with the results obtained from the state-of-the-art equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method.

Theoretical Study on Merger of Photoredox and Transition Metal Catalysis

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The photoredox/transition metal dual catalysis has become a hot research topic in the development of photochemical reactions and functional materials. This strategy provides access to non-traditional fundamental organometallic steps. Density functional theory (DFT) calculations have been performed to explore the detailed mechanism of photoredox/Ni-catalyzed carbon–nitrogen cross-coupling. The Ni(0) catalyst initiates the C–N cross-coupling and the photocatalyst *[Ir(III)]+ engages the Ni(II) complex in single-electron transfer (SET). The pathway of the Ni(I) catalyst initiating the catalytic cycle is prohibited due to the relatively high activation barrier of the oxidative addition of the aryl bromide to the Ni(I) catalyst. It is predicted that the Ni(II) salt is reduced by pyrrolidine through the mechanism of photoredox-catalyzed hydrogen atom transfer (HAT). The mechanistic insights could be helpful in the further development of the rational design of new catalysts and reactions. Recently, we also studied the enhancement of visible-light absorption and catalytic efficiency through the rational modification of metal-organic frameworks (MOFs).

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Nonadiabatic Dynamics and Machine Learning

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Our works focus on the theoretical description of nonadiabatic dynamics on molecular excited states. In this talk, I will outline a few of our important progresses in last few years.

1. We will discuss the framework of trajectory surface hopping (TSH) and the implementation of the TSH in the on-the-fly simulation. We introduced the supervised machine-learning (ML) approaches into the nonadiabatic dynamics simulation. The nonadiabatic Zhu-Nakamura TSH dynamics simulation was run using potential energy surfaces (PESs) based on kernel-ridge-regression technique.
2. We show the possibility to analyze the geometrical evolution of trajectory-based nonadiabatic molecular dynamics by the unsupervised machine learning and big data analysis, particularly the dimensionality reduction techniques (Classical Multidimensional Scaling and Isometric Mapping). These approaches allow us to extract the major molecular motion from the very complicated time-dependent evolution from many trajectories without pre-knowledge of reaction pathway of excited state reactions.
3. We will also discuss out recent work on the symmetrical quasiclassical dynamics in the basis of mapping Hamiltonian.

A new perspective for nonadiabatic statistics and dynamics

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Based on the recently developed unified theoretical framework, we propose a new perspective for studying nonadiabatic dynamics with classical mapping models (CMMs) of the coupled multi-state Hamiltonian onto the Cartesian phase space. CMMs treat the underlying electronic state degrees of freedom classically with a simple physical population constraint while employing the linearized semiclassical initial value representation to describe the nuclear degrees of freedom. We have tested various benchmark condensed phase models where numerically exact results are available, which range from finite temperature to more challenging zero temperature, from adiabatic to nonadiabatic domains, and from weak to strong system-bath coupling regions. CMMs demonstrate overall reasonably accurate dynamics behaviors in comparison to exact results even in the asymptotic long time limit for various spin-boson models and site-exciton models. Further investigation of the strategy used in CMMs may lead to practically useful approaches to study nonadiabatic processes in realistic molecular systems in condensed phase.

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3. X. He and J. Liu, J. Chem. Phys. 151, 024105 (2019) [Invited contribution to the Special Topic Issue on "Dynamics of Open Quantum Systems"]

Biography

Jian Liu obtained B.S. (2000) from the University of Science & Technology of China and then Ph.D. (2005) from the University of Illinois at Urbana-Champaign. He worked as a postdoctoral fellow at the University of California, Berkeley (2005-2011) and then as a research associate at Stanford University (2011-2012), before he was appointed Associate Professor at the College of Chemistry and Molecular Engineering, Peking University (2012-present). His research interests has focused on the development of theories and methodologies of quantum/semiclassical dynamics and quantum statistics for complex/large molecular systems. Liu was a recipient of the American Chemical Society Physical Chemistry Division Postdoctoral Research Award (2012), the Chinese National "Thousand Young Talents Program" fellowship (2012), the Chinese Chemical Society Tang Au-Qing Youth Award on Theoretical Chemistry (2015), the 2018 QSCP Promising Scientist Prize of CMOA (Centre de Mécanique Ondulatoire Appliquée), and the 2019 Pople Medal of the Asia-Pacific Association of Theoretical and Computational Chemists. Liu has been a member of the Editorial Advisory Board of The Journal of Physical Chemistry since 2017.

Topology of quantum coherence network in singlet fission

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Exciton singlet fission, in which a singlet exciton transforms into two triplet excitons, has attracted rapidly increasing interests in the research community in recent years. Not only being proposed as a potential boost to the existing solar cell technologies, singlet fission also offers a great opportunity to explore quantum dynamics in complex systems, in which multiexcitation state, superexchange mechanism, and many-body interactions, all could play a vital role in modulating quantum coherence and quantum dynamics. Although intensive and extensive investigations have been devoted to unraveling molecular mechanisms of singlet fission and to establishing rational design principles of new materials, most exiting works focus on specific effects on fission dynamics or efficiency while the global analysis on the multi-dimensional quantum dynamics is largely unexplored. As an extension to our recent work on the topology of quantum coherence in singlet fission, quantum coherence network (QCN) is proposed to provide a global picture on quantum coherence in high dimensional multistate systems. Incorporating molecular specific properties, QCN can be formed based on basic elements including energy levels, interstate couplings, etc. And taking nonadiabatic molecular dynamics simulation of singlet fission in tetracene clusters as a case study, we will show that the topology of QCN could help characterize the global structure of multistate systems, which may inspire new strategies for modulating quantum dynamics in complex systems, and for materials design.

Keywords

Quantum coherence; singlet fission; global structure; nonadiabatic dynamics; materials design.

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Onsets of dissipaton equation of motion theory

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Dissipaton equation of motion (DEOM) theory [1] is a fundamental method for open quantum systems, with quasi-particle descriptions on Gaussian environment influences. Beside its recovering the well-known HEOM formalism [2,3], the DEOM theory explicitly treats also the hybrid bath dynamics [4-6]. The underlying essential dissipaton algebra includes the generalized diffusion equation and the generalized Wick's theorem [1] that is rooted at the system-bath entanglement theorem [7]. To complete the quasi-particle descriptions, we recently identified further the phase-space disspaton algebra [6]. This enables the accurate DEOM evaluations on such as solvation phase-space dynamics and nonequilibrium heat transport problems. It is also anticipated that the phase-space DEOM theory be a solid starting formalism for the further development of various DEOM-based exact and semiclassical methods. If time permits, I will also discuss the all-first-principles studies on realist single-molecular spintronic systems [8], which combine the DEOM dynamics and the conventional electronic structural determinations.

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Quantum localization and delocalization of charge carriers in organic semiconducting crystals

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Charge carrier transport in organic semiconductors is at the heart of many revolutionary technologies ranging from organic transistors, light-emitting diodes, flexible displays and photovoltaic cells. Yet, the nature of charge carriers and their transport mechanism in these materials is still unclear. Here we show that by solving the time-dependent electronic Schrödinger equation coupled to nuclear motion for eight organic molecular crystals, the excess charge carrier forms a polaron delocalized over up to 10–20 molecules in the most conductive crystals.[1] The polaron propagates through the crystal by diffusive jumps over several lattice spacings at a time during which it expands more than twice its size. Computed values for polaron size and charge mobility are in excellent agreement with experimental estimates and correlate very well with the recently proposed transient localization theory.

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Excited State Dynamics in Hybrid Materials for Solar Energy Harvesting

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Excited state dynamics play key roles in numerous novel molecular and nanoscale materials designed for photovoltaics, photocatalysis, electronics, spintronics and many other applications. Controlling these far-from-equilibrium processes and steering them in desired directions require understanding of material's dynamical response on the nanometer scale and with fine time resolution. We couple real-time time-dependent density functional theory for the evolution of electrons with non-adiabatic molecular dynamics for atomic motions to model such non-equilibrium response in the time-domain and at the atomistic level.

The talk will describe the basics and recent advances of the simulation methodology and will discuss several exciting applications among the broad variety of systems and processes studied in our group, including hybrid organic/inorganic perovskites, transition metal dichalcogenides, semiconducting and metallic nanoparticles and films, molecular crystals, organic polymers, graphene, carbon nanotubes, etc. Photo-induced charge and energy transfer, Auger-type processes, energy losses and charge recombination create many challenges due to large differences between molecular and periodic, and organic and inorganic matter. Our simulations provide a unifying description of quantum dynamics on the nanoscale, characterize the timescales and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems.

Finite Temperature Time Dependent Density Matrix Renormalization Group for Exciton-Phonon Model

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We present our recent advances in developing finite temperature time-dependent DMRG for molecular aggregates based exciton-phonon coupling model, which is a many body problem for phononic states. We introduce a hybrid TD-DMRG/TDHartree algorithm for even larger degrees of freedom. We present a comparative study on the accuracy and efficiency for three time evolution schemes: the direct propagation and compression with 4th order Runge-Kutta propagator (P&C-RK4), the time dependent variational principle with matrix unfolding (TDVP-MU) and the projector splitting (PS) on the exciton dynamics. We show that the PS scheme is the most accurate and the fastest method because the propagation in each step is unitary by combining Krylov subspace algorithm and there is no error caused by regularization or instability of matrix inversion. We also compare the parallelization efficiency of multi-core central processing units (CPU) with graphical processing units (GPU) and we find that although 28 cores of CPU can merely double the speed, GPU is able to speedup the TDVP-MU and PS scheme by up to 57 times through efficient acceleration of matrix multiplication. Using the optimal strategy, we are able to simulate the full quantum exciton dynamics for a 7-site FMO model with 252 degrees of freedom to a timescale of 1 ps at fairly high accuracy within only 4 minutes.

Integrating Machine Learning and Multi-Layer Energy-based Fragment Method for Excited States and Nonadiabatic Dynamics

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We recently 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] Very recently, we have also combined machine learning (ML) techniques with MLEBF[2-3]. The photochemically active and inert regions are separately treated with the complete active space self-consistent field (CASSCF) method and trained ML models. This ML-MLEBF method also 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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Machine Learning and Semiempirical Methods for Nonadiabatic Dynamics

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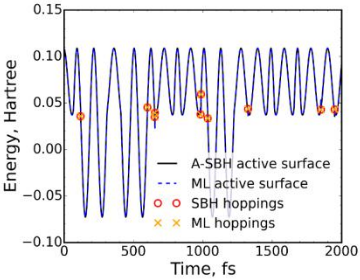
We have suggested several approaches for reducing the staggering computational cost of the decoherence-corrected fewest-switches surface hopping technique for nonadiabatic excited-state molecular dynamics (NA-MD).

One of them is to use machine learning (ML) for calculating the properties necessary for NA-MD, *i.e.* energies, gradients, and couplings. For small model systems ML can exactly reproduce the reference dynamics (see Figure).[1] For larger realistic models, the reference results can be reproduced with small loss of accuracy given enough training points. If ML has accurate information on the conical intersection (CX) region from training data, pure ML dynamics can be performed, otherwise reference QC calculations have to be invoked in CX regions.[1-3] We are currently preparing the release of an interface between *Newton-X* (performing NA-MD)[4-5] and *MLatom* (performing ML calculations)[6-7] for running ML-NA-MD.



Another approach to reduce the cost of QC calculations is using efficient low-cost semiempirical QC methods (SQC) for running NA-MD.[8] To this end, we have recently introduced two new SQC methods, ODM2 and ODM3, which are to-date the most accurate NDDO-based SQC methods for a broad variety of properties including ground-state and excited-state properties.[9] The ODM2 and ODM3 methods are promising candidates for performing large-scale NA-MD simulations as is currently explored.

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Poster

Analytical calculation of the exciton dynamics in a vibrationally coupled homodimer based on the polaron transformation

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Abstract: Experiments on light-harvesting systems have revealed long-lived coherences in electronic 2D spectra, whose origin is still being debated at present [1-2]. It has been suggested that these coherences can be explained by a vibrational coupling of the excitonic states. Numerical methods have been applied which confirm this conjecture using particular sets of parameters, yet, analytical understanding is still lacking.

The polaron-transformed Redfield equation has been developed in recent years, which is an analytical approach to describe the exciton dynamics from weak to strong system-bath coupling on equal footing [3-4]. We apply the polaron transformation to analytically calculate the linear absorption and the 2D electronic spectrum of a homodimer, at which the excitonic states are coupled to local vibrational modes. We show how the linear absorption and the 2D spectra are composed of contributions of the vibrational modes, the vibronic eigenstates, and multi-time bath correlation functions.

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Strong solid-state fluorescence induced by restriction of the coordinate bond bending in two-coordinate Copper(I)-carbene complexes

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The photophysical properties of two-coordinate copper(I) complexes have become a new research hotspots due to its nearly perfect luminescent property and low price and promising applications in organic light-emitting diodes (OLEDs). In this work, we employ the hybrid quantum mechanics and molecular mechanics (QM/MM) approach coupled with our early developed thermal vibration correlation function (TVCF) rate formalism, to study the aggregation effect on the luminescent properties of the cyclic-(alkyl)(amino)-carbene-copper(I)-Cl complex. Our calculations reveal that the transition properties changes from metal-ligand-charge-transfer (MLCT) in solution to hybrid halogen-ligand-charge-transfer (XLCT) and MLCT in solid state, which induces the blue shifted emission spectra from solution to solid phase. Upon aggregation, the restriction of the bending vibrations of the C-Cu-Cl and Cu-C-N bonds largely slow down the nonradiatve decay, which induces strong fluorescence. This study provides a clear rationalization for the highly efficient fluorescence character of two-coordinate Cu(I) complexes.

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Theoretical study on the charge carrier transport dynamics in organic molecular crystals using the Nakajima-Zwanzig-Mori generalized master equation

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There has been a long history of applying the generalized master equation (GME) to study charge carrier and exciton transport in molecular systems. Yet exact memory kernels in the GME are generally difficult to obtain. In this work, exact memory kernels of the Nakajima-Zwanzig-Mori GME for a one-dimensional Holstein type of model are calculated by employing the Dyson relation for the exact memory kernel, combined with the hierarchical equations of motion method. Characteristics of the exact memory kernels, as well as the transition rate constants within the Markovian approximation are then analyzed for different sets of parameters ranging from the hopping to band-like transport regimes. It is shown that, despite the memory effect of the exact kernels, the Markovian approximation to the exact GME can reproduce the diffusion constants accurately. We also investigate the validity of the second and fourth order perturbation theories in calculating the rate constants and the diffusion constant. It is found that, due to the cancellation of errors, the second order diffusion constant gives a reasonable estimate of the exact one within a wide range of electronic coupling constants.

Keywords: Generalized master equation; HEOM; Holstein model; charge transport

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A novel multiscale continuum electric double-layer model for electron-proton interplay at the TiO_2/electrolyte interface

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Recent years have seen much progress in developing novel photovoltaics, photoelectrochemical systems and optoelectronics. We have developed multiscale device models to study several emerging optoelectronic materials such as organic solar cells, nanostructured solar cells, plasmonic solar cells, and photoelectrochemical systems. The interaction between excess electrons from bulk semiconductors and protons from aqueous electrolytes at the semiconductor/electrolyte interface is crucial to determine the interfacial behaviors of photoelectrochemistry. Here, we develop a novel multiscale continuum electric double-layer (CEDL) model (e.g. for the rutile TiO_2 (110)/$KClO_4$ interface) to study the interfacial distributions of charge and electric field, and investigate the effect of interfacial electron-proton interplay on the surface Pourbaix diagram and (non-)Nernstian pH dependence of potential for the first water oxidation step. The newly developed CEDL model tightly combines the continuum medium model for charge transport in the semiconductor and electrolyte, with the interfacial thermodynamic characteristics of water oxidation reactions. Based on the quantum mechanically calculating key parameters for the CEDL model, our simulations validate that the interfacial electron-proton interplay plays an essential role in the acid dissociation and oxidation reactions in the surface Pourbaix diagram, but not affect the dehydrogenation reaction owing to the Helmholtz double potential. In addition, we can optimize the physicochemical conditions (e.g. semiconductor doping level, Helmholtz layer capacitance and solution pH) for the first water oxidation step with lower thermodynamic overpotentials at the semiconductor/electrolyte interface, by exploring the effect of interfacial electron-proton interplay on the (non)-Nernstian dependence. We convince that the pH dependence of water oxidation potential at the whole

range of pH does not necessarily follow the Nernstian behavior. The CEDL model in this work opens up more possibilities for theoretical studies of the interfacial photoelectrochemistry.

A Full Picture of Enzymatic Degradation of the G-Type Nerve Agent by Phosphotriesterase: Revised Role of Water Molecules and Rate-Limiting Product Release

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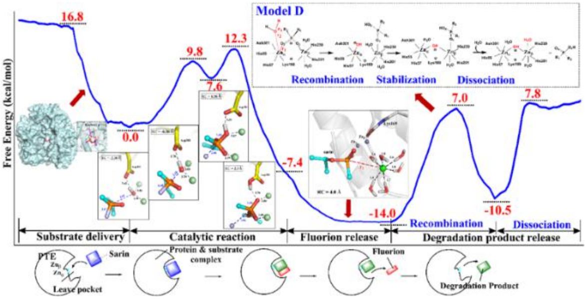
Nerve agents are highly toxic organophosphorus compounds, and the wild-type phosphotriesterase (PTE) enzyme is capable of hydrolyzing these organophosphates but with a low catalytic efficiency. Here the whole enzymatic detoxification process of the G-type nerve agent sarin by the PTE enzyme, including the substrate delivery, the chemical reaction, and the product release, has been explored by extensive QM/MM MD and MM MD simulations. The plausible mechanisms for the chemical and nonchemical steps, the roles of water molecules, and the key residues have been discussed. The enzymatic P−F cleavage of sarin is a two-step exothermic process with the free-energy span of 12.3 kcal/mol, and it should be facile in the whole enzymatic catalysis. On the contrary, the initial degraded product is tightly bound to the binuclear zinc center, and its dissociation experiences multiple chemical steps with the free-energy barriers of 21.0 kcal/mol for the recombination process and 18.3 kcal/mol for the release of the product phosphoester from the active site. The side-chain residues Leu271 and Phe132 in the transportation channel function as the entrance gate in PTE and play an important gate-switching role to manipulate the substrate access to the active site and the product release. These mechanistic details for the enzymatic degradation of sarin by PTE provide significant clues to improve its activity toward the nerve agents.



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Excited States of Intermediates and Radicals from the Pyrolysis of Furan Molecules: A Theoretical Insight

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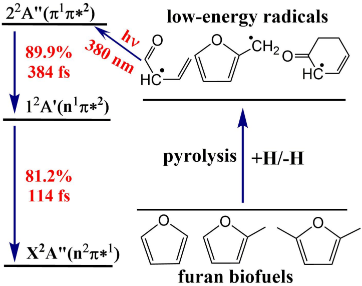
Extensive density functional theory and sophisticated wave function theory calculations have been performed to explore the ground-state properties as well as the low-lying valence excited states and Rydberg states of the radical species, which are generated from the pyrolysis of furan biofuels. The most easily formed stable radicals are predicted to be 1-C_4H_3O-3, 1-C_4H_5O-2, and furylCH$_2$, respectively. Some among the electronic excitations to low-lying states can take place in the visible light region, and they may be involved in the combustion process. Further surface hopping dynamics simulations of the two low-lying excited states of the most stable ring-opening radical 1-C_4H_5O-2 of furan have been performed, and the results suggest that the reactive radicals in the ground state are mainly responsible for the combustion chemistry of furan biofuels.



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Persulfurated Coronene and Its Chalcogenide Analogues: Insight into Effects of the Peripheral Substitution on Electronic and Spectroscopic Properties

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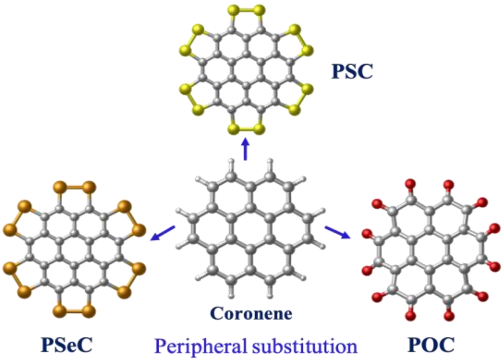
The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods have been used to investigate the persulfurated coronene (PSC) and its chalcogenide analogues (POC and PSeC), derived from the substitution of sulfur, oxygen, and selenium for all hydrogen atoms in coronene, respectively. The presence of peripheral S-S in PSC results in a σ-type lowest unoccupied molecular orbital (LUMO) and the dark low-lying states ($S_1 \sim S_{15}$). The peripheral S-S bond is responsible for its electron capture, which maintains a planar configuration of the singly and doubly negative-charged PSC. POC is predicted to have the most stable saddle-shaped structure with the C=O group. PSeC has similar electronic and structural features with PSC, but its dimer is predicted to have much better hole mobility, compared to PSC. The present results indicate that the chalcogenide substitution at the periphery of the polycyclic aromatic hydrocarbons may remarkably change their electronic and spectroscopic properties as well as the carrier transport behavior of their molecular materials.



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Analysis of Electronic Properties of Planarized Triphenylamines

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We performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations to analyze electronic properties and explain experimental observations for a series of planarized triphenylamines[1] related to the systems we studied earlier.[2-4] Our calculations showed that the ionization energies are not strongly affected by adding electron-withdrawing groups to the triangulene core, because the Kohn–Sham HOMOs are mostly localized on this core.

To elucidate the nature of the absorption bands in the experimentally recorded UV/vis spectra, we performed TD-DFT calculations with various range-separated functionals. The electronic excitations were characterized as localized or charge-transfer states by analyzing the one-electron transition density matrix (1TDM)[5] as implemented in the TheoDORE program package.[6] For this, we split the system into four parts: the triangulene core and three electron-withdrawing groups.

Since using the default range separation parameter in TD-DFT calculations has led to unsatisfying results, we optimize this parameter to get better agreement between simulated and experimental UV/vis spectra. We use the procedure described in literature[7] and the optDFTw program.[8]

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Structure and property tunability in monolayer halide lead-free double hybrid perovskites: effects of Rashba and biaxial strain

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Organic–inorganic metal hybrid perovskites (OIMHPs) are playing increasingly important roles in the development of stable and lead-free perovskite materials. Metal halide perovskites(MHPs) possess fascinating properties like optimal band gaps for harvesting sunlight, high optical absorption, high charge-carrier lifetimes, low effective carrier masses and long diffusion lengths, etc. [1-6] However, while the center Pb atoms are substituted, most of them are indirect-band semiconductors with large band gaps[7] which severely limit their development for practical applications. [8-9]

Here we theoretically investigate the intrinsic structures/properties and biaxial strain-induced changes for the monolayer lead-free OIHDP, $MA_4[AgBi]Br_8$ (MA = $CH_3NH_3^+$), and propose to use strain to tune its electronic structures and so optimize its properties.

Our results reveal that pristine $MA_4[AgBi]Br_8$ has an indirect band gap originated in the inequality of spin–orbit coupling (SOC) effects on its valence and conduction band extrema and on two directions around the high symmetry point of the Brillouin zone as well, and that the strain tunes the band gap and the Rashba effect, and as a result it mediates the band structure. The band gap of $MA_4[AgBi]Br_8$ varies linearly with the strain ratio and a ≥2% stretching can turn it into a complete direct-band semiconductor. $MA_4[AgBi]Br_8$ shows different properties under various strain conditions. Compression strengthens the giant SOC-related characteristics including the SOC-induced indirect band gap and Rashba band-splitting, while moderate stretching not only lessens the band gap but also can enhance the carrier mobility and exciton separation.

These results indicate that $MA_4[AgBi]Br_8$ has the potential to be a stable and non-toxic multifunctional perovskite material. This work also provides some full-scale insights into the Rashba effect on band structures and the correlation between structures/properties and the strain ratio.

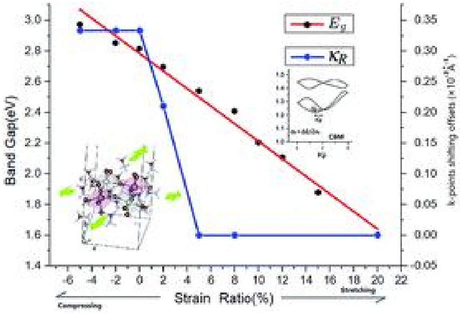

Fig. The band properties of $MA_4[AgBi]Br_8$ varies with strain ratio

Keywords： keyword； keyword； keyword （Up to 5 keywords）

Funding：National Science Foundation of China (Grant No. 21573177 and 21833006)

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Collaborative Effect of Plasmon-Induced Resonance Energy and Electron Transfer on the Interfacial Electron Injection Dynamics of Dye-Sensitized Solar Cell

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It has been widely-recognized that plasmonic metal nanoparticles (MNPs) can enhance the power convention efficiency (PCE) of dye-sensitized solar cells (DSSCs). PIRET[1] and HEI[2,3] processes appeared between MNPs and semiconductors have been intensively investigated.
In this work, we apply a model Hamiltonian method, which obviously includes both PIRET and PICT processes from Au MNP to dye molecules and incorporates the dye's electron-phonon interaction, to investigate the carrier dynamics. It is found that PIRET deforms the wavepacket dynamics of the molecular excited state and results in ten-fold enhancement of dye absorption. MNPs augment light absorption and increase the electron density in empty molecular orbitals of the dye molecule. Consequently, this enhances the interfacial charge separation. Furthermore, we observed the interference behavior of two CSCs and gave a full-scale insight into the correlation between the constructive/destructive interference and the electronic-state properties as well as carrier-phonon interactions. This work provides a theoretical guidance to optimize DSSCs.

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The Vibronic Absorption Spectra and Exciton Dynamics of Plasmon-Exciton Hybrid Systems in the Regimes Ranged from Fano Antiresonance to Rabi-like Splitting

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The complex interplay between molecules and plasmonic metal nanoparticles (MNPs) presents a set of particular characteristics in absorption/scattering spectra such as excitonic splitting[1], asymmetric lineshapes[2], plasmon-induced absorption enhancement and transparencies[3], etc.

In this work, we present a theoretical approach which can account for both the plasmon-exciton coupling and the e-p interaction, and produce all the spectral lineshapes ranged from Fano antiresonance to Rabi splitting by simply tuning the coupling strength or plasmon damping rate. Additionally, we demonstrate the evolution of vibronic spectra and exciton dynamics with the coupling strength, plasmon damping rate and the detuning energy. It is found that the vibronic structures appeared in Rabi-like spectra are worse resolved, wider and more largely shifted than those appeared in Fano regime, attributed to the more significant deformation of the molecular vibrational wavepacket in Rabi-like regime than in Fano regime as the molecular e-p interaction increases. The positive/negative value of detuning energy can induce different degrees of the vibrational wavepacket deformation, subsequently different effect on the spectra in different coupling regimes.

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Insights into the Mechanism of Fatty Acid Photodecarboxylase:

Trimolecular vs. Bimolecular Photocycle

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Recently a new photoenzyme, fatty acid photodecarboxylase (FAP), was reported by Beisson *et al.* that can catalyze fatty acid decarboxylation to afford *n*-alkanes or *n*-alkenes in blue light.[1] A trimolecular photocycle mechanism involving an unidentified proton donor HX was proposed, which is seemingly incompatible with the observed high quantum yield (> 80%), as the quantum yields of trimolecular photoreactions reported thus far are extremely poor.[2-3] Herein, we propose an alternative bimolecular mechanism, in which the photoactive part of FAD cofactor in FAP, i.e., the lumiflavin (Fl) fragment (Fig.1), can be protonated to work as proton donor. Our molecular model-based density functional calculations disclosed that the bimolecular photocycle can proceed smoothly in five steps, i.e., photoexcitation of FAD, proton transfer from carboxylic acid to the excited state of FAD, electron transfer from carboxylate anion to the protonated FAD*, decarboxylation and hydrogen abstraction, energetically more favorable than the previously proposed trimolecular mechanism. The present study indicates that the light-capturing organic molecule, lumiflavin (Fl) of FAD, can act as a metal-free photocatalyst for the photodecarboxylation of fatty acids to afford hydrocarbons, which is yet relatively rare in organic synthesis.[4-7]

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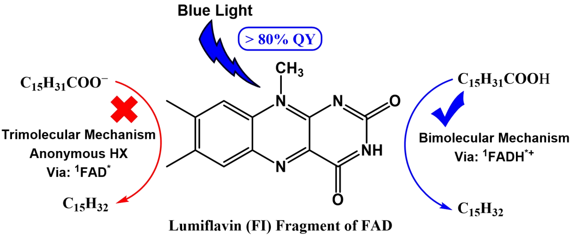

Fig. 1: Comparison of two photodecarboxylation mechanisms of fatty acid photodecarboxylase

Theory Demonstrated a “Coupled” Mechanism for O2 Activation and Substrate Hydroxylation by Binuclear Copper Monooxygenases

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Multiscale simulations have been performed to address the longstanding issue of the “dioxygen activation” by the binuclear copper monooxygenases (PHM and DβM), which were traditionally classified as the “noncoupled” binuclear copper enzymes. Our QM/MM calculations rule out that CuM(II)-O2• is an active species for H-abstraction from the substrate. By contrast, CuM(II)-O2• would abstract an H atom from the co-substrate ascorbate to form a CuM(II)-OOH intermediate in PHM and DβM. Consistent with the recently reported structural features of DβM, the umbrella sampling shows that the “open” conformation of CuM(II)-OOH intermediate could readily transform into the “closed” conformation in PHM, in which we located a mixed-valent μ- hydroperoxodicopper(I,II) intermediate, (μ-OOH)Cu(I)Cu(II). The subsequent O-O cleavage and OH moiety migration to CuH generate an unexpected species of (μ-O•)(μ-OH)Cu(II)Cu(II), which is revealed to be the reactive intermediate responsible for substrate hydroxylation. We also demonstrate that the flexible Met ligand is favorable for O-O cleavage reaction, while the replacement of Met with the strongly bound His ligand would inhibit the O-O cleavage reactivity. As such, the study not only demonstrates a “coupled” mechanism for O2 activation by binuclear copper monooxygenases, but also deciphers the full catalytic cycle of PHM and DβM in accord with the available experimental data. These findings of O2 activation and substrate hydroxylation by binuclear copper monooxygenases could expand our understandings on the reactivities of the synthetic mono-copper complexes.

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The molecular mechanisms of oxygen activation and hydrogen peroxide formation in lytic polysaccharide monooxygenases

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The recently discovered lytic polysaccharide monooxygenases (LPMOs) are copper-dependent enzymes for the degradation of recalcitrant polysaccharides such as chitin and cellulose. Unlike classical hydrolytic enzymes (cellulases), LPMOs catalyze the cleavage of the glycosidic bond via an oxidative mechanism using oxygen and a reductant. The full enzymatic molecular mechanisms, starting from the initial electron transfer from a reductant to oxygen activation and hydrogen peroxide formation, are not yet understood. Using QM/MM metadynamics simulations, we have uncovered the complete oxygen activation mechanisms by LPMO in the presence of ascorbic acid, one of the most used reductants in LPMOs assays. Our simulations capture the sequential formation of $Cu(II)-O_2^-$ and $Cu(II)-OOH^-$ intermediates via facile H-atom abstraction from ascorbate. By investigating all the possible reaction pathways from the $Cu(II)−OOH^-$ intermediate, we ruled out $Cu(II)-O\bullet^-$ formation via direct O-O cleavage of $Cu(II)-OOH^-$. Meanwhile, we identified the exclusive pathway in which the proximal oxygen atom of $Cu(II)−OOH^-$ abstracts a hydrogen atom from ascorbate, leading to Cu(I) and H_2O_2. The "in situ" generated H_2O_2 either converts to $LPMO-Cu(II)-O\bullet^-$ via a homolytic reaction, or diffuses into the bulk water in an uncoupled pathway. The competition of these two pathways is strongly dependent on the binding of the carbohydrate substrate, which plays a role in barricading the "in situ" generated H_2O_2 molecule, preventing its diffusion from the active site into the bulk water. Based on the present results, we propose a new catalytic cycle of LPMOs that is consistent with the experimental

information available. In particular, it explains the enigmatic substrate-dependence of the reactivity of the LPMO with H_2O_2.

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Adsorption, Stretching and Breaking Processes on Metal- Molecule-Gold Junctions: A DFT-NEGF Study

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Single-molecule junction displays potential power due to its small size and multi-mode functions. To gain deep insight into the electrical and mechanical properties of molecular junctions,the gold-*para*-benzenedimethanethiol (BDMT)-gold molecular junction with different binding configurations has been investigated by using density functional theory (DFT) combined with non-equilibrium Green's function (NEGF) approach.

To consider the symmetrical change of the molecular binding structures at both anchor ends, the dynamic evolutions under pulling are simulated by two methods, i.e., one-end stretching and two-end stretching. By estimating broken forces at different binding configurations, we found that the Au-Au bond broken at top and bridge sites when the sulfur atoms bind to the gold single crystal surface, however, the Au-S bond breaking only occurs at a four-atom pyramid structure with a tip shape. For interfacial configurations at the top and bridge sites, the molecular conductance first has an exponential decrease, and then a flat platform, and finally a directly going-down decrease under pulling process of molecular junctions. For the gold tip, the double-end stretching results in the conductance producing a sharply increase before the complete breaking state. This can be understood due to the site-site interaction in the molecule, which is sufficiently strong to drive the single-molecule junction close to resonance tunneling. Our results revealed the detailed correlation of structure and molecular conductance upon stretching processes. The conductance-distance curves reproduce the trends observed in the experiments well, indicating that the single molecular conductance changes closely associated with dynamic stretching processes.

DFT Study for SERS of Sulfanilamide Adsorbed on Metal Surfaces of Nanostructures

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Surface Enhanced Raman Spectroscopy (SERS) is a powerful method to identify molecular fingerprint information for qualitative and quantitative analysis of molecules and structural characterization of molecules[1]. Sulfonamides, as a class of antibiotics, have been widely used in the world for decades, and it accounts for a large part of the pharmaceutical industry[1]. Sulfadiazine and p-aminobenzene sulfonamide (PABS) as the most basic molecules in sulfanilamide antibiotics, the development of detection methods has attracted extensive attention. Based on quantum mechanics and density functional theory (DFT), we have been calculated the molecule structures of sulfadiazine in aqueous solution and interfaces of nanoparticles. Then we also simulated the SERS spectra of sulfadiazine adsorbed on metal surface (as shown in Fig. 1i). Finally, we further considered that the metal nanoparticle may activate the adsorbed molecules on metal surface. For example, laser induces such molecules taking place a photocatalytic reaction. We found that the PABS might occur a catalytic coupling reaction to produce azo compound, and its Raman spectrum as shown in Fig. 1ii) is in agreement with experimental spectra [2].

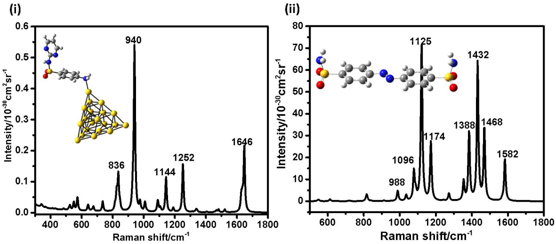

Figure1. Theoretical SERS spectrum of sulfadiazine (i) and the Raman spectrum of PABS azo compound (ii)

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Two-Dimensional Analysis of Diabatic Transition of General Vectorial Physical Observable Based on Adiabatic-to-Diabatic Transformation

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Performing the adiabatic-to-diabatic transformation using physical observables is an effective way to obtain diabatic states. In this work, we carry out a full analysis on both the magnitude and orientation of the diabatic transition matrix element of a general vectorial physical observable during the adiabatic-to-diabatic transformation. Furthermore, it is also very useful for determining the adiabatic-to-diabatic transformation angle, and evaluating the quality of various approximations in constructing the diabatic states.

Energy decomposition analysis based on broken symmetry unrestricted density functional theory

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A new extension of generalized Kohn-Sham energy decomposition analysis (GKS-EDA), called GKS-EDA(BS), is present for intermolecular interactions in open-shell singlet states, which is a challenge for existing EDA methods due to the multi-reference character. Combining with broken symmetry unrestricted density functional theory (BS-UDFT), GKS-EDA (BS) divides the total interaction energy into electrostatic, exchange, repulsion, polarization, correlation, and dispersion terms. Test examples, including the pancake bond in the phenalenyl dimer, the ligand interactions in the Fe(II)-porphyrin complexes and the radical interactions in dehydrogenated Guanine-Cytosine base pairs, show that the nature of intermolecular interaction in open-shell singlet states can be quite different from those in closed-shell singlets.

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Photo-dissociation of formaldehyde:
A valence bond study

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In this poster, we present the use of valence bond theory in providing chemical pictures for potential energy surfaces in photochemical reactions. The mechanism for the photo-dissociation of formaldehyde into H_2 and CO has been investigated by ab initio VB method. The excitation energies and wave function in the ground state and the $n \rightarrow \pi^*$ excited state along the pathway are discussed. The properties of the reaction in conical intersections are investigated. It is found that the mechanism of the photo-reaction involves three steps of intramolecular electron transfer, which finally lead to stable dissociation products H_2 + CO.

Non-Markovian stochastic Schrödinger equation in k-space toward the calculation of carrier dynamics in organic semiconductors

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A non-Markovian stochastic Schrödinger equation developed in our former work [Y. Ke and Y. Zhao, J. Chem. Phys. 147, 184103 (2017)] is extended to the reciprocal (k-) space to calculate the carrier dynamics in organic semiconductors with both local and nonlocal carrierphonon interactions taken into account. The validity of this approach is examined by comparing with numerically exact benchmark results. As an application, the carrier mobilities are calculated within a one-dimensional periodic lattice model. The results reveal an inversion in the magnitude of the mobility as the nonlocal carrier-phonon interaction varies from weak to strong strengths, indicating a transition of the transport mechanism. This is also demonstrated by a variation in the temperature dependence of the mobility. In addition, a transient localization diffusive behavior caused by intramolecular vibrations is also found.

Convolutional neural networks for the design and analysis of non-fullerene acceptors

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Convolutional neural network (CNN) is employed to construct the generative and prediction models for the design and analysis of non-fullerene acceptors (NFAs) in organic solar cells. It is demonstrated that the dilated causal CNN can be trained as a good string-based molecular generation model and the diversity of generated NFAs is influenced by the depth of convolutional layers. In the property prediction model, the features of NFAs are extracted from the string representations by the dilated CNN. Specially, the attention mechanism is adopted to pool the extracted information, from which the contributions of fragments to molecular properties can be obtained by calculating the corresponding weighted sum. The promising NFAs among the predicted molecules are further verified by quantum chemistry calculations. The proposed generative, prediction models and the theoretical calculations perform as a complete cycle from molecular generation, property prediction to verification, which offers a strategy for the application of CNN in material discovery.

Variational polaron transformation approach toward the calculation of the thermopower in organic crystals

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Based on the combination of the variational polaron transformation and the Green-Kubo formalism, a method toward the thermopower calculations in organic crystals is proposed, which covers a broad regime of electron-phonon interaction strengths and successfully recovers the small-polaron theory in the narrow-band limit and the modified Mott formula in the coherent limit, respectively. The application to a molecular chain reveals a crossover of the thermopower with respect to the chemical potential and exhibits abnormal regions where the sign of the thermopower is opposite to the sign of the carrier charge. This abnormal property may lead to a sign-inversion phenomenon of the thermopower in terms of the temperature. It is also found that the incomplete dressing of the electron by the phonon cloud destroys the particle-hole symmetry and results in a nonzero thermopower in a half-filled band.

Dual σ-Aromaticity in the Lowest Singlet and Triplet States: Tetraatomic Boron Species with a Triplet Ground State Character*

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In comparison with widely recognized π -aromaticity, σ-aromaticity is a less developed concept in chemistry, especially for the unsaturated system. Moreover, most studies on the σ-aromaticity have been mainly limited to the ground state of saturated systems1, unsaturated species with σ-aromaticity in the excited state has never been reported. Here we demonstrate that the recently synthesized tetraatomic boron species is σ-aromatic not only in the lowest singlet state but also in the lowest triplet state according to density functional theory (DFT) calculations, supported by numerous aromaticity indices, such as nucleus independent chemical shift (NICS), anisotropy of the induced current density (ACID), and electron density of delocalized bonds (EDDB)2-4. In addition, several isomers are found to possess a triplet ground state character. Our findings highlight the importance of developing the concept of σ-aromaticity in unsaturated systems, which are traditionally reserved as the domain of π-aromaticity.

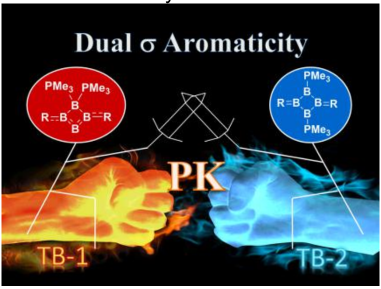

Figure-1. Dual σ-aromaticity of tetraatomic boron species in the lowest singlet and triplet states.

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* Financial support by the National Science Foundation of China (21873079)

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Designing Singlet Fission Materials via Excited-State Aromaticity[*]

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Singlet fission is a photophysical process in which an organic chromophore transforms a high-energy excited singlet exciton into two low-energy excited triplet excitons. It can reduce the energy loss when the single junction solar cell absorbs high-energy photons to improve the photoelectric conversion efficiency of solar cells[1]. Therefore, the design of novel high efficiency single fission materials has attracted widespread attention from experimental[1] and computational[2] chemists in recent years. However, it is particularly limited[3] to use the Baird rule of excited state aromaticity to help design novel singlet fission materials. Inspired by the recent work of the Bronstein group[3] and in combination with our interest in excited-state aromaticity[5], here we will probe the aromaticity and substituent effects on singlet fission properties of heteronaphthalenes by DFT calculations.

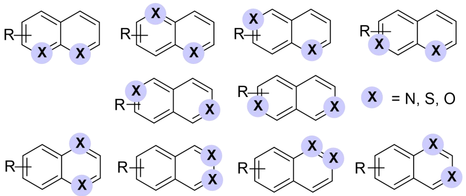

Figure 1. in the proposed heteronaphthalenes for singlet fission

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[*] Financial support by the National Science Foundation of China (21873079).

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Adaptive Aromaticity of Osmapyridinium with Carbone Ligands*

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Aromaticity is a fundamental concept in chemistry. Because of its versatile application, it has attracted extensive attention of experimentalists and theoreticians. According to Hückel's and Baird's rules, cyclic conjugated compounds are aromatic either in the ground state or in the excited states. Recently, our group reported the first example of aromaticity in both S0 and T1 states (adaptive aromaticity)1 in 2018. Further, the first example (osmapyridinium with phosphonium substituents) with a triplet ground state and adaptive aromaticity2 was reported this year. On the other hand, carbone (CL2) with a divalent C0 atom retains its four valence electrons as lone-pairs and is capable of binding two neutral donor ligands L with dative bonds3. Here, we demonstrate that osmapyridinium with carbone (CL2) possesses adaptive aromaticity by DFT calculations, which is supported by various aromaticity indices including ΔBL, HOMA, ELFπ, MCI, ACID and the heat of hydrogenation.

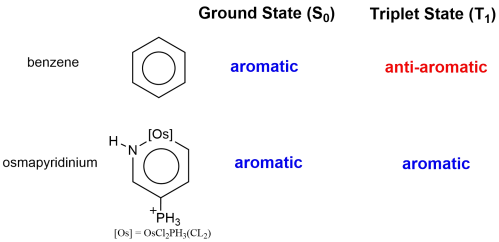

Figure 1. Aromaticity of benzene and osmapyridinium with carbone ligands (CL_2) in S_0 and T_1 states

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