

CSRC Workshop on Quantum Coherence in Energy Transfer and Conversion

Sept.18-20, 2018 Beijing China

Date & Location

Date: Sept.18-20 , 2018

Venue: Conference Room I, 1st Floor, CSRC Building, Beijing

Contact Information

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Free Wi-Fi_{csrc_guest}

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PROGRAM AT A GLANCE

Sept.18 (Tuesday)	Sept.19 (Wednesday)	Sept.20 (Thursday)
Registration 8:30-9:10 Talk 9:10-12:00	Talk 9:00-12:00	Talk 9:00-12:00
Talk 14:00-17:00	Talk 14:00-17:00	Talk 14:00-16:00
Poster Session 17:00-17:30	Banquet	

Program

All invited talks are 40 minutes including questions. The talks are arranged according to the topics.

 **Tuesday, Sept. 18**

 **Room: Conference Room I, First Floor**

8:30-9:10 Registration

9:10-9:15 Welcome

9:15-9:25 Remarks by CSRC director, Prof. Haiqing Lin

9:30-10:20 Classical Molecular Dynamics Simulations of Electronically Non-Adiabatic Processes

keynote lecture by Prof. Bill Miller (University of California, Berkeley)

10:20-10:40 *coffee break*

10:40-11:20 Including nuclear quantum effects in mixed-quantum classical non-adiabatic dynamics

Tom Miller (California Institute of Technology)

11:20-12:00 An Exact Approach for Quantum Statistics of Multi-Electronic-State Systems

Jian Liu (Peking University)

12:00-2:00 *lunch break*

2:00-2:40 First Principles Model Hamiltonian Ensembles for Light Harvesting: Signatures of Coherent Excitonic and Vibronic Energy Transfer in Non-linear 2DES Signals

David Coker (Boston University)

2:40-3:20 Multiscale dynamics of energy transfer in light-harvesting protein complexes from FMO to PSII

Jianlan Wu (Zhejiang University)

3:20-3:40 *Coffee break*

3:40-4:20 Quantum coherence in the dynamics of biomolecular excitons - revisited

Michael Thorwart (Universität Hamburg)

4:20-5:00 Quantum transport on lattices and complex networks

Daniel Mazano (University of Granada)

5:00-5:30 Poster Session

 **Wednesday, Sept. 19**

 **Room: Conference Room I, First Floor**

9:00-9:40 **Tracing feed-back driven exciton dynamics in molecular aggregates**

Leonas Valkunas (Vilnius University)

9:40-10:20 **Coherent Quantum Transport in Molecular Aggregates and Light-Harvesting Systems**

Jianshu Cao (Massachusetts Institute of Technology)

10:20-10:40 *Coffee Break*

10:40-11:20 **Quantum mechanics of open systems: A statistical quasi-particle**

Yijing Yan (USTC)

11:20-12:00 **Semiclassical Approximations with Coherent States**

Jiushu Shao (Beijing Normal University)

12:00-2:00 *lunch break (group photo)*

2:00-2:40 **Excited states processes in molecular aggregates**

Zhigang Shuai (Tsinghua University)

2:40-3:20 **Charge carrier transport and charge separation dynamics in organic semiconductors: Theoretical studies based on model systems**

Qiang Shi (Chinese Academy of Sciences)

3:20-3:40 *Coffee break*


3:40-4:20 **Controllable quantum dissipative dynamics of a two-level system**

Hang Zheng (Shanghai Jiao Tong University)

4:20-5:00 **Controlling Energy Transport and Fluctuation in Nonequilibrium Spin-Boson Systems**

Jie Ren (Tongji University)

Workshop Banquet

 **Thursday, Sept. 20**

 **Room: Conference Room I, First Floor**

- 9:00-9:40** **Tensor train algorithms for quantum dynamics simulations of excited state nonadiabatic processes and quantum control**
Victor Batista (Yale University)
- 9:40-10:20** **Quantum Phase Transition and coherent state transfer between qubits coupled to a quantum cavity**
Stefano Chesi (Beijing Computational Science Research Center)
- 10:20-10:40** *Coffee Break*
- 10:40-11:20** **Theory of open quantum systems and quantum thermodynamics**
Wei-Min Zhang (National Cheng Kung University)
- 11:20-12:00** **Quantum coherence in heat conversion: efficiency at maximum power, true steady state and strong coupling regime**
Konstantin Dorfman (East China Normal University)
- 12:00-2:00** *lunch break*
- 2:00-2:40** **Exciton Seebeck Effect and Exciton Interference in Molecular**
Yun-An Yan (Ludong University)
- 2:40-3:20** **Quantum thermal transport through anharmonic systems: A self-consistent approach and its applications**
Daihai He (Xiamen University)
- 3:20-3:40** **Coherent energy transfer probed by quantum measurement and response theory**
Houdao Zhang (USTC)
- 3:40-4:00** **How misuse of thermodynamics potentials can lead to "thermodynamic inconsistencies"**
Zhedong Zhang (IQSE, Texas A&M University)

Abstracts

Tensor train algorithms for quantum dynamics simulations of excited state nonadiabatic processes and quantum control

Victor S. Batista

Yale University, Department of Chemistry & Energy Sciences Institute

Abstract

We introduce the “tensor-train split-operator Fourier transform” (TT-SOFT) algorithm for simulations of multidimensional nonadiabatic quantum dynamics [*J. Chem. Theory Comput.* **13**: 4034-4042 (2017)]. TT-SOFT is essentially the grid-based SOFT method implemented in dynamically adaptive tensor-train representations. In the same spirit of all matrix product states, the tensor-train format enables the representation, propagation, and computation of observables of multidimensional wave functions in terms of the grid-based wavepacket tensor components, bypassing the need of actually computing the wave function in its full-rank tensor product grid space. We demonstrate the accuracy and efficiency of the TT-SOFT method as applied to propagation of 24-dimensional wave packets, describing the S_1/S_2 interconversion dynamics of pyrazine after UV photoexcitation to the S_2 state. Our results show that the TT-SOFT method is a powerful computational approach for simulations of quantum dynamics of polyatomic systems since it avoids the exponential scaling problem of full-rank grid-based representations. The development of ultrafast laser technology has also opened the possibility to control ultrafast reaction dynamics in excited electronic states. Thus, we report a Floquet theoretical study of quantum control of the ultrafast cis-trans photoisomerization dynamics of rhodopsin [*J. Chem. Theory Comput.* **14**(3): 1198-1205 (2018)]. The predicted light-induced potentials, including light-induced conical intersections, can open new reaction channels or modify the product yields of existing pathways. The nonadiabatic dynamics is described by a 3-state 2-dimensional wave-packet, coupled to a bath of 23 vibrational modes, evolving according to an empirical model Hamiltonian with frequencies and excited-state gradients parameterized to reproduce the observed resonance Raman excitations of rhodopsin. We analyze the effect of different control pulses on the photoisomerization dynamics, including changes in pulse duration and intensity. We interpret the results in terms of 'dressed states' and we exploit the Floquet description where the effect of control pulses is naturally decoupled along the different channels. Results obtained with 300 fs-long pulses suggest that it should be possible to delay the excited-state isomerization for hundreds of femtoseconds. Our findings are thus particularly relevant to the development of ultrafast optical switches based on visual pigments.

Quantum Coherence in Light-harvesting Systems and Organic Semiconductors

Jianshu Cao

Department of Chemistry, MIT

Abstract

Quantum coherence is a key concept in chemical physics and will be discussed in the context of charge mobility/exciton diffusion in organic semiconductors and energy transfer in light-harvesting complexes.

I. Coherent quantum transport in disordered systems displays an optimal diffusion constant at an intermediate level of noise and temperature. [1] Detailed calculations indicate the crucial role of localization length in coherent transport and predict charge mobility close to experimental values. [2] Further, we have explored the subtle dependence of the diffusion constant on the dimensionality and shape of the sample and demonstrated the universal scaling of the 1D-2D transition in nanotubes. [3]

II. Forster energy transfer theory has been extended to multi-chromophoric (MC) systems by incorporating the correlation between exciton and its environments. This correlation leads to the rotation of the reduced density matrix and is fully counted in two recently-developed methods: numerically exact stochastic path integrals (SPI) [4] and theoretically self-consistent coherent potential approximation (CPA) [5]. Application of these methods demonstrates incoherent hopping in FMO [6] and coherent transfer in LH2 [7].

References:

1. Moix, Khasin, Cao, *New Journal of Physics*, 15, 085010 (2013)
2. Lee, Moix, Cao, *J. Chem. Phys.* 142, 164103 (2015)
3. Chuang, Lee, Moix, Knoester, and Cao, *Phys. Rev. Lett.* 116, 196803 (2016)
4. Moix, Ma, Cao, *J. Chem. Phys.* 142, p094108 (2015)
5. Chenu and Cao, *Phys. Rev. Lett.* 118, 013001 (2017)
6. Wu, Liu, Ma, Silbey, and Cao, *J. Chem. Phys.* 137, 174111 (2012); Moix, Wu, Huo, Coker, J. Cao, *JPC Letts.* 2, 3045 (2011)
7. Cleary and Cao, *NJP* 15, p05030 (2013); Moix, Ma, and Cao, to be submitted (2018)

Quantum Phase Transition and coherent state transfer between qubits coupled to a quantum cavity

Stefano Chesi

Beijing Computational Science Research Center

Abstract

We discuss two topics concerning qubits coupled to a quantized cavity mode. In the first part of the talk we consider the quantum state transfer between qubits, with the cavity acting as a quantum bus. Focusing on the limit of a strong photon losses, we optimize quasi-adiabatic protocols which are able to minimize the excitation of the quantum bus. In order to provide physical insight on such protocols, we have pursued an analytical treatment with full consideration of system dissipation, and derived an upper bound on the fidelity. We find that the optimized fidelity and transfer time are a simple functions of the system cooperativity, and we also provide a systematic approach to reach this upper bound efficiently. In the second part of the talk, we investigate the quantum phase transition of the anisotropic quantum Rabi model, in which a single qubit interacts with the cavity. Having rotating- and counter-rotating terms with different coupling strengths allows us to investigate the issue of universality in few-body quantum phase transitions. Our findings are relevant in a variety of systems able to realize strong coupling between matter and light, including circuit QED and semiconductor qubits coupled to microwave resonators.

First Principles Model Hamiltonian Ensembles for Light Harvesting: Signatures of Coherent Excitonic and Vibronic Energy Transfer in Non-linear 2DES Signals

David Coker

Boston University

Abstract

Accurate model Hamiltonians for excitation energy transfer, including vibronic transitions, in a variety of pigment-protein complexes are parameterized, using Molecular Dynamics and first principles calculations. Semi-classical methods for computing non-linear 2D electronic spectra for these models are presented and employed to explore the signatures of excitonic and vibronic energy transfer in these systems. Results are analyzed in terms of simple models for electronic and vibronic decoherence dynamics.

Quantum coherence in heat conversion: efficiency at maximum power, true steady state and strong coupling regime

Konstantin E. Dorfman¹

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Abstract

Various quantum effects have been observed in the thermodynamic of small systems. For instance understanding the microscopic origin of the quantum coherence and its role in the energy and charge transfer processes along with thermodynamics characteristics of the small systems is a key problem in both thermodynamics and quantum mechanics. We survey several effects associated with the quantum coherence and interference and their effects on steady state and transient behavior of the quantum heat engines (QHE), e.g. lasers, photovoltaic cells [1], photosynthetic reaction centers [2], and nanoplasmonic devices [3]. We showed that the maximum power of a QHE that converts incoherent thermal energy into coherent cavity photons could be enhanced by manipulating quantum coherences. We demonstrated that in both artificial (solar cells) and natural (photosynthesis) light harvesting coherence affects the same population–coherence coupling term which is induced by bath (e.g. phonons), does not require coherent light, and will therefore work for incoherent excitation under natural conditions of solar excitation. We further investigate a novel model of the three-level laser QHE [4] where lasing occurs between two closely spaced metastable states and the ground state. Engine operates by transferring energy from hot bath to cold bath via nonequilibrium coherence assisted process. Coherence has two sources: first is due to quantum interference generated via hot bath and second is due to the lasing field coupled to both metastable states. The resulting efficiency at maximum power may be improved due to interplay between these two coherence contributions. Finally, we investigated the strong system-bath coupling beyond Master equation approach using polaron frame to show how the strong coupling affects the thermodynamics of the heat engine. Various parameter regimes are considered.

Reference

1. M.O. Scully, K. Chapin, K.E. Dorfman, M. Kim, and A.A. Svidzinsky, PNAS **108**, pp. 15097-15100, (2011).
2. K.E. Dorfman, D.V. Voronine, S. Mukamel, and M.O. Scully, PNAS, **110**, 2746 (2013).
3. K.E. Dorfman, P.K. Jha, D.V. Voronine, P. Genevet, F. Capasso, and M.O. Scully, Phys. Rev. Lett. **111**, 043601 (2013).
4. K.E. Dorfman, D. Xu, and J. Cao, Phys. Rev. E **97**, 042120 (2018).

Quantum thermal transport through anharmonic systems: A self-consistent approach and its applications

Dahai He

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Abstract

Developing a first-principles based approach for quantum thermal transport across low-dimensional systems not only provides insight to potential nano-device applications, but is also crucial to better understand nonequilibrium statistical physics. To date, quantum thermal transport across harmonic crystals has been extensively studied. However, it is still a challenging problem to deal with thermal transport in a system of strong anharmonicity, which is nevertheless one of the key ingredients for interesting practical applications. In this talk, I will introduce a feasible and effective approach to study quantum thermal transport through anharmonic systems. The main idea is to obtain an effective harmonic Hamiltonian for the anharmonic system by applying the self-consistent phonon theory. As its application, I will show the role of system-bath coupling strength on quantum interfacial thermal transport thanks to the phonon delocalization effect.

References:

- [1] D. He, J. Thingna, J.-S. Wang and B. Li, *Phys. Rev. B* **94**,155411(2016).
- [2] D. He, J. Thingna, and J. Cao, *Phys. Rev. B* **97**,195437(2018).

An Exact Approach for Quantum Statistics of Multi-Electronic-State Systems

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Abstract

An exact approach to compute physical properties for general multi-electronic-state (MES) systems in thermal equilibrium is presented.[1] The approach is extended from our recent progress on path integral molecular dynamics (PIMD) [2,3] for quantum statistical mechanics when a single potential energy surface is involved. We first define an effective potential function that is numerically favorable for MES-PIMD, and then derive corresponding estimators in MES-PIMD for evaluating various physical properties. Its application to several representative one-dimensional and multi-dimensional models [1,4] demonstrates that MES-PIMD in principle offers a practical tool in either of the diabatic and adiabatic representations for studying exact quantum statistics of complex/large MES systems when the Born-Oppenheimer approximation, Condon approximation, and harmonic bath approximation are invalid.

References

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2. Jian Liu, Dezhang Li, Xinzijian Liu. (2016). Journal of Chemical Physics, 145, 024103
3. Zhijun Zhang, Xinzijian Liu, Zifei Chen, Haifeng Zheng, Kangyu Yan, Jian Liu. (2017). Journal of Chemical Physics, 147, 034109
4. Haobin Wang, Xinzijian Liu, Jian Liu. (2018). Chinese Journal of Chemical Physics, 31, 446

Quantum transport on lattices and complex networks

Daniel Manzano Diosdado

University of Granada

Abstract

Quantum transport in lattices is a major field of study nowadays. It has been probed that a lattice composed by harmonic oscillators connected to two thermal baths at different temperatures behaves ballistically in any dimension [1]. On the other hand, if the lattice is composed by spins it is ballistic only in the one-dimensional case [2, 3]. In the simplest two-dimensional spin lattice, a ladder, it has been numerically probed the existence of both ballistic and non-ballistic channels [4].

In this talk, I show that both fermionic and bosonic uniform d-dimensional lattices can be reduced to a set of independent one-dimensional chains [5]. This reduction leads to the expression for ballistic energy fluxes in uniform fermionic and bosonic lattices. By the use of the Jordan-Wigner transformation, we can extend our analysis to spin lattices, proving the coexistence of both ballistic and non-ballistic subspaces in any dimension and for any system size. We then relate the nature of transport to the number of excitations in the homogeneous spin lattice, indicating that a single excitation always propagates ballistically and that the non-ballistic behaviour of uniform spin lattices is a consequence of the interaction between different excitations.

Finally, we will also discuss the role of symmetries in complex compounds and their transport properties. Symmetry is a key concept in quantum mechanics and it plays an important role in many systems found in Nature, including many biological systems as photosynthetic complexes. Recently, the implications of symmetries and transport properties have been reviewed [6]. Recently, a technique based in measuring quantum currents to find signatures of symmetries has also been developed [7].

In this talk we will discuss the implications of symmetries in biological complexes and their transport properties. We will also discuss how to detect symmetries in unknown molecular systems by the use of a simple and realistic framework.

References:

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- [6] D. Manzano and P. I. Hurtado. Advances in Physics (in press). arXiv:1707.07895v2.
- [7] J. Thingna, D. Manzano, and J. Cao. Scientific Reports 6, 28027 (2016)

Classical Molecular Dynamics Simulations of Electronically Non-Adiabatic Processes

William H. Miller

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Abstract

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

Including nuclear quantum effects in mixed-quantum classical non-adiabatic dynamics

Thomas F. Miller III

Professor of Chemistry, Division of Chemistry and Chemical Engineering, California Institute of Technology

A focus of my research is to develop simulation methods that reveal the mechanistic details of quantum mechanical reactions that are central to biological, molecular, and heterogeneous catalysis. The nature of this effort is three-fold: we work from the foundation of quantum statistical mechanics and semiclassical dynamics to develop methods that significantly expand the scope and reliability of condensed-phase quantum dynamics simulation [1]; we develop quantum embedding and machine learning methods that improve the description of molecular interactions and electronic properties; and we apply these methods to understand complex chemical systems.

In this talk, we describe a path-integral approach for including nuclear quantum effects in non-adiabatic chemical dynamics simulations [1,2]. For a general physical system with multiple electronic energy levels, a corresponding isomorphic Hamiltonian is introduced, such that Boltzmann sampling of the isomorphic Hamiltonian with classical nuclear degrees of freedom yields the exact quantum Boltzmann distribution for the original physical system [1]. In the limit of a single electronic energy level, the isomorphic Hamiltonian reduces to the familiar cases of either ring polymer molecular dynamics (RPMD) or centroid molecular dynamics Hamiltonians, depending on implementation. An advantage of the isomorphic Hamiltonian is that it can easily be combined with existing MQC dynamics methods, such as surface hopping or Ehrenfest dynamics, to enable the simulation of electronically non-adiabatic processes with nuclear quantum effects.

References:

- [1] "Ring polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space." S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, *Annu. Rev. Phys. Chem.*, 64, 387 (2013).
- [2] "Kinetically constrained ring-polymer molecular dynamics for non-adiabatic chemical reactions." A. R. Menzeleev, F. Bell, and T. F. Miller III, *J. Chem. Phys.*, 140, 064103 (2014).
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Controlling Energy Transport and Fluctuation in Nonequilibrium Spin-Boson Systems

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Abstract

In this talk, I would like to review our recent works on controlling thermal transport and fluctuation in nonequilibrium spin-Boson systems. I first introduce the nonequilibrium Spin-Boson model where the central spin system is coupled to external bosonic thermal reservoirs, and the full counting statistic theory that counts the high order fluctuations for the nonequilibrium thermal transport. In the second part, I introduce the some interesting nonequilibrium phenomena in spin-boson model, like the heat diode, Berry-phase induced heat pump, and the negative differential thermal conductance. However, contradiction exists between the strong and weak spin-boson coupling limit. Thus, we develop a generalized nonequilibrium polaron-transformed Redfield equation to unified describe the transport in spin-boson model across from weak to strong spin-boson coupling. In the last part, if time is allowed, I will extend the present discussions to Fermion-Spin-Boson systems.

Charge carrier transport and charge separation dynamics in organic semiconductors: Theoretical studies based on model systems

Qiang Shi

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Abstract

I will present some recent progresses in our group in theoretical studies of charge carrier transport and charge separation dynamics in organic semiconductors using model systems: (1) Application of the generalized master equation (GME) to study the charge carrier and exciton transport in molecular systems. In this work, exact memory kernels of the Nakajima-Zwanzig GME for a one dimensional Holstein type of model are calculated by using 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 also give accurate diffusion constants. (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 identified, 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. The current results indicate that only a small energy offset between the band gap and the lowest energy CT state is needed to achieve efficient free charge generation in OPV devices, which agrees with recent experimental findings.

References:

- [1] Y.-M. Yan, L.-Z. Song, and Q. Shi, *J. Chem. Phys.* 148, 084109 (2018).
- [2] Y.-M. Yan, M. Xu, Y.-Y. Liu, and Q. Shi, in preparation.

Excited states processes in molecular aggregates

Zhigang Shuai

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Abstract

We developed a rate based formalism to calculate the lowest excited state decay rates (radiative and non-radiative). Combined with (TD)DFT calculations, we revealed the mechanism of the exotic optical phenomenon for molecular aggregates: Aggregation-Induced Emission and Room temperature Organic Phosphorescence. Then we present a time dependent density matrix renormalization group theory (TD-DMRG) as a non-perturbative method to calculate the linear absorption and fluorescence spectra of molecular aggregates by explicitly treating the electronic and vibrational degrees of freedom together at both zero and finite temperature. The validity of this method is benchmarked by comparing with other existing methods in both model and real systems, which demonstrates that TD-DMRG is an accurate, efficient and robust method to calculate the spectrum of molecular aggregates. We further developed a multi-scale quantum simulation method: TD-DMRG/TD-Hartree method which is applicable for complex quantum dynamics system.

Quantum coherence in the dynamics of biomolecular excitons - revisited

Michael Thorwart

Universität Hamburg

Abstract

The harvest of solar photon energy is at the heart of photosynthesis in large biomolecular complexes or of man made solar cell devices. After a photon has delivered its energy in the form of an exciton, the nonequilibrium quantum dynamics of this quasiparticle transports the energy to a reaction center where chemical reactions are triggered. These first steps of photosynthesis are accessible by ultrafast optical spectroscopy on the femtosecond time scale. Experiments have challenged the traditional picture of a mostly incoherent exciton dynamics between different molecular sites and a supportive role of quantum coherence for the transfer efficiency has been suggested, despite the ubiquitous “hot and wet” disturbing environment.

I will show how quantum coherence of biomolecular excitons is influenced by environmental noise stemming from polarization fluctuations of the solvent under ambient conditions and from the vibrational motion of the molecular backbone [1-4]. In particular, I will report recent theoretical and experimental results [5] on optical 2D photon echo spectra of the Fenna-Mathews-Olson complex at ambient temperature in aqueous solution. They do not provide evidence of long-lived electronic nor strong vibronic quantum coherence, but confirm the orthodox view of rapidly decaying quantum coherence on a time scale of 60 fs under ambient conditions. Corresponding calculations at low temperature yield a dephasing time of 120 fs at a temperature of 77 K. Our results can be considered as generic and give no hint that electronic quantum coherence plays any biofunctional role in real photoactive biomolecular complexes [6]. Since this natural energy transfer complex is rather small and has a structurally well defined protein with the distances between bacteriochlorophylls being comparable to other light-harvesting complexes, we anticipate that this finding is general and directly applies to even larger photoactive biomolecular complexes.

References:

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Tracing feed-back driven exciton dynamics in molecular aggregates

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Abstract

Perturbative treatment of excitation dynamics in molecular systems with respect to external interactions to the dissipative environment is extensively used for the description of excitation energy transfer and relaxation. However the simulated dynamics becomes sensitive to the specific representation basis set, what makes the outcoming conclusions obscure and questionable. We revisit questions of excitation creation pattern, coherent dynamics, relaxation and detection from theoretical viewpoint, and demonstrate that a mixture of specific requirement should be met to observe coherent phenomena and incoherent decay processes. We discuss how intermixing of coherent components in relaxation phenomena are related to non perturbative regime of dynamics leading to non linear feed-back effects where bath relaxation also affects excitation wavepackets. We also discuss how the bath equilibration causes local heating effects what is often neglected in numerical simulations. The parameters reflecting the complexity of the processes are related to excitation delocalization patterns in various basis representations. While these seem to be an auxiliary non observable features, their evaluation allow to better inspect the physical behavior of quantum relaxation process in molecular aggregated systems.

Multiscale dynamics of energy transfer in light-harvesting protein complexes from FMO to PSII

Jianlan Wu, Zhoufei Tang and Ze Zhan

Zhejiang University

Abstract

Due to the spatial separation of pigments in light-harvesting protein complexes, an energy transfer process often occurs in multiple time scales from femtoseconds to hundreds of picoseconds. A quantitative description of multiscale quantum dynamics requires a picture of spatially aggregated clusters (or domains). At the second order, multichromophoric Forster theory (MCFT) has provided successful predictions in various light-harvesting systems such as LHII. Through the development of cluster-based generalized quantum kinetic expansion (GQKE) method, we built a formally exact framework for both cluster and site dynamics. With the facilitation of the hierarchy equation of motion (HEOM), we numerically calculated quantum kinetic rates in light-harvesting systems from FMO to PSII.

Quantum mechanics of open systems: A statistical quasi-particle approach

YiJing Yan

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Abstract

In this talk, I will present the dissipaton-equation-of-motion (DEOM) [1], a fundamental and statistical quasiparticle theory in quantum mechanics (including quantum thermodynamics) of open systems. Not only it recovers the hierarchical equations of motion formation [2,3], the new theory also identifies the auxiliary density operators to the quasi-particles dynamics of hybridizing bath [1]. The DEOM theory unifies the treatments on three distinct classes of environments, electron bath, phonon bath, and exciton (two-level spin) bath. It provides an accurate and versatile means in characterizing strongly correlated system and hybridization bath dynamics. Induced bath dynamics could be reflected directly in experimentally measurable quantities, such as Fano resonances and quantum transport current noise spectrum. Some benchmark evaluations on strongly correlated systems will be presented [4-6]. Recent advancements include further a comprehensive theory of quantum dissipation in a class of non-Gaussian coupling environment [7].

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Exciton Seebeck Effect and Exciton Interference in Molecular Aggregates

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Abstract

The hierarchical approach (HA) is a standard method to simulate the exciton dynamics. In the HA and other schemes for simulating autonomous systems, the dynamics is dictated by linear differential equations with constant coefficients. Although simple in mathematical concept, the integration of these equations is usually complicated in practice for complex systems, where both the computational time and the memory storage become limiting factors. In this talk we first presents our work for the low-storage explicit Runge-Kutta methods specific for autonomous linear equations, which only requires two times of the memory storage for the state vector. Then, we show the effects of the temperature difference and quantum interference simulated with the low-storage implementation for the HA.

The temperature difference causes exciton population redistribution and affects the exciton transfer time. It is found that one can reproduce not only the exciton population redistribution but also the change of the exciton transfer time induced by the temperature difference with a proper tuning of the site energies of the aggregate. In this sense, there exists a site energy shift equivalence for any temperature difference in a broad range. This phenomenon is similar to the Seebeck effect as well as spin Seebeck effect and is named as exciton Seebeck effect.

We have also found that the exciton quantum interference could be significant in aggregates. The exciton transfer time only shows a weak excitation energy dependence for models with single-path bridge. But models with double-path bridge present a new short transfer time scale and the excitation energy dependence of the exciton transfer time assumes clear peak structure which is detectable with today's nonlinear spectroscopy. This abnormality is attributed to the exciton quantum interference. It is revealed that the exciton interference could be easily observed in the aggregates with a donor having a long homogeneous chain structure, a nearly degenerate two-path bridge, and weak inter-site vibrational correlation.

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Coherent energy transfer probed by quantum measurement and response theory

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Abstract

Coherent Energy Transfer (ET) plays an important role in photosynthetic and photovoltaic systems. Multidimensional spectroscopy experiments have shown that even at room temperatures, electronic coherence can survive for hundreds of femtoseconds [1,2]. However, coherent versus incoherent effects in ET should be identified based on the evolution of the reduced system density matrix, whereas the notions of coherence, as well as population, are basis-set-dependent. A basis-set-independent characterization of coherent effects in ET is still to emerge. We suggest an approach, based on diagonalization of the reduced system density matrix at all times, attributing the changes in the time-dependent eigenvalues and eigenvectors to incoherent and coherent processes, respectively. Adopting the above view, both limiting cases of Förster and Redfield ET are completely incoherent, since in both cases, the basis sets are almost maintained throughout the evolution, being just the site and exciton basis sets, respectively. Only the most complex case of comparable vibronic and electronic coupling shows substantial coherent effects.

We explore the possibility of monitoring coherent energy transfer using single-molecule measurements. This necessarily involves the Quantum Measurement (QM) theory due to the quantum nature of coherent energy transfer and repeated character of a single-molecule measurement. Adopting a Weak Measurement (WM) concept, we derive a version of a stochastic trajectory formalism that is very close to an experiment in a lab setting, by dealing with the probabilities of continuous electrical current measurement in the detector [3-6]. We show that the correlation functions of the measured currents, available from statistical processing of experimental data, contain detailed information on the reduced density matrix evolution, and further develop response theory for multi-time correlation functions. This response theory is analogous to the standard optical response counterpart [7], with one interesting difference: the role of the driving field is also played by the QM via its intrinsic property to affect the measured system.

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Theory of open quantum systems and quantum thermodynamics

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Abstract

Based on the exact master equation theory we developed for quantum systems interacting with environments through the exchanges of matter, energy and information, we investigate nonequilibrium thermodynamics to arbitrary small quantum systems, even for single particle systems. With the generalized concept of “temperature” in nonequilibrium regime, we find (i) the emergence of classical thermodynamics from quantum dynamics in the weak system-reservoir coupling regime, without introducing any hypothesis on equilibrium state; (ii) the breakdown of classical thermodynamics in the strong coupling regime, induced by non-Markovian memory dynamics; and (iii) the occurrence of negative temperature associated with dynamical quantum phase transition. The corresponding dynamical criticality provides the border separating the classical and quantum thermodynamics, associated with inflationary dynamics that may relate to the origin of universe inflation. The third law of thermodynamics, allocated in the deep quantum realm, is naturally proved in this theory.

How misuse of thermodynamics potentials can lead to "thermodynamic inconsistencies"

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Abstract

In an interesting recent paper [1], it was incorrectly claimed that the results of our analysis [2] violate the second law of thermodynamics. They then offer a suggestion on how to “fix it”. We here show the error in their analysis and counter that: “if it ain’t broke, don’t fix it”.

Quantum thermodynamics is a subtle blend of quantum and classical thermodynamics physics. For example, the Kelvin–Planck statement of the second law of thermodynamics: Any amount of work can be turned into heat, but heat cannot be totally converted to work. However, Ramsey showed that with the existence of negative temperature, the Kelvin-Planck statement of the second law can be violated.

It is therefore important to carefully analyze all such problems and to properly understand the thermal and quantum physics. Recently, a study [1] claimed that a possible violation of the second law of thermodynamics exists in a widely used model of natural light-harvesting and solar cell. However, we find that, such seeming violation roots from some subtle difference of two concepts: the total energy output and the useful work output. It is known that the energy output is often accompanied by entropy output, therefore, not all the output energy can be used for work. Only part of the output energy can be used to produce chemicals or perform work. Based on the solar cell model, we here show how to calculate the useful output work, which has the familiar form of free energy, and satisfies the second law.

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Controllable quantum dissipative dynamics of a two-level system

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Abstract

We investigate the quantum dissipative dynamics of a two-level system (qubit) by means of the modulation of an assisted tunneling degree of freedom which is described by a quantum-oscillator spin-boson model. Our results reveal that the decoherence rate of the qubit can be significantly suppressed and simultaneously its quality factor is enhanced. Moreover, the modulated dynamical susceptibility exhibits a multi-peak feature which is indicative of the underlying structure and measurable in experiment. Our findings demonstrate that the interplay between the combined degrees of freedom and the qubit is crucial for reducing the dissipation of qubit and expanding the coherent regime of quantum operation much large. The strategy might be used to fight against deterioration of quantum coherence in quantum information processing.

Posters

Molecular Vibrational Spectroscopy Study by Path Integral

Liouville Dynamics

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Abstract

The normal-mode analysis (NMA) and molecular dynamics are often inadequate for studying the molecular vibrational spectroscopy where anharmonicity is significant [1]. Path integral Liouville dynamics (PILD), a novel imaginary time path integral-based dynamics approach that we have recently developed [2], is able to give accurate vibrational spectra for real molecules, e.g. OH, H₂O, NH₃, and CH₄ [3]. In this work we continue with several molecules which are often studied as benchmark calculations. Comparison to the exact vibrational frequency shows that PILD produces a reasonably accurate peak position with a relatively small full width at half maximum.

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Tuning the Aharonov-Bohm effect with dephasing

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The Aharonov-Bohm (AB) effect, which predicts that a magnetic field strongly influences the wave function of an electrically charged particle, is now investigated in a molecular junction setup. The AB effect leads to a non-monotonic dependence of the steady-state current on the gauge phase associated with the molecular ring. This dependence is sensitive to site energy, temperature, and dephasing, and can be explained using the concept of the dark state. Although implications of the phase effect vanish in the steady-state current for strong dephasing, the phase dependence becomes visible in an associated waiting-time distribution, especially at short times. Interesting, the phase rigidity (i.e., the symmetry of the AB phase) observed in the steady-state current is now broken in the waiting-time statistics, which can be explained by the interference between transfer pathways.

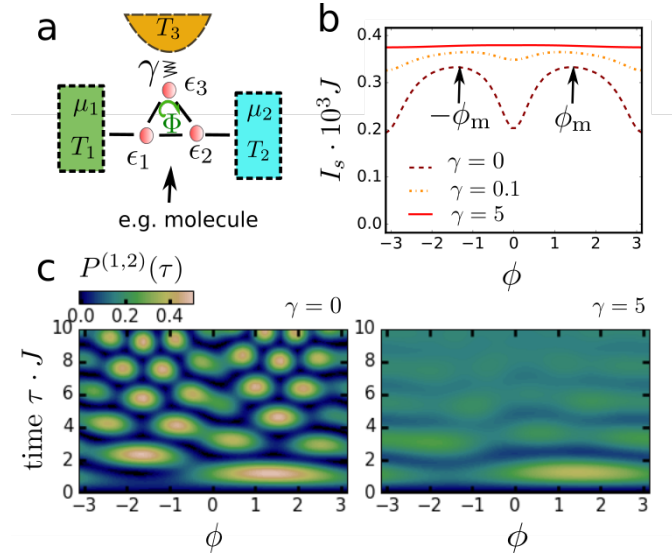


Figure : (a) A molecular junction described by three sites $n = 1, 2, 3$ which are connected to two electronic leads $n = 1, 2$ and a thermal bath $n = 3$. (b) Current as a function of the phase ϕ . (c) Waiting time distribution of two consecutive jumps in and out of the system.

Rational Construction of Operator Splitting Methods for Path Integral Molecular Dynamics

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Path integral molecular dynamics (PIMD), which is based on imaginary time path integral, offers a convenient computational technique for studying structural and thermodynamic properties of general molecular systems when quantum statistical effects are important. Fourth order decompositions of the imaginary time path integral propagator are developed in order to improve the convergence of estimators for physical observables as a function of the number of beads, while the standard path integral method employs a second order decomposition. We propose a new fourth order decomposition, and compare the conventional second order scheme and the new fourth order scheme in the PIMD simulations. The results of the PIMD simulations of the realistic system (liquid water) show that our new scheme performs more efficiently than the second order scheme for achieving the same accuracy.

Keywords: path integral molecular dynamics; operator splitting method; Langevin dynamics.

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Diverse Isotope Effect for Charge Transport: A DMRG Study

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The isotope effect (IE) on charge transport was proposed in 1970¹ to judge the transport mechanism. However, there had not been a definitive answer for nearly 50 years as to whether such an IE is positive or negative, both theoretically and experimentally, because either theory was too approximate or the experimental estimate was too rough to make a judgment². Employing time-dependent density matrix renormalization group method (TD-DMRG)³, we investigate the IE by simulating the diffusion of charge based on a one-dimensional molecule chain Holstein model in both band and hopping limit at finite temperature. The method has the advantage of including the quantum effect of nuclear vibrations inherently which is particularly important for inspecting IE. We show that isotope substitution has diverse influence on charge transport at different regime. In band limit where the effect of phonon can be neglected, IE does not affect charge transport; In hopping limit substitution of heavier isotopes leads to negative IE; whereas in the intermediate regime a positive IE is observed.

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Decisive Role of Quantum dynamical effects in the Raman spectroscopy of liquid water

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Understanding the Raman spectroscopy at the atomistic level is important for the elucidation of dynamical processes in liquid water.^[1-3] We have done quantum/semiclassical simulations of liquid water and heavy water under ambient conditions using an ab initio-based, polarizable model (POLI2VS)^[4]. It is shown that quantum dynamical effects play a decisive role in reproducing the intermediate region between the librational and bending bands, that between the bending and stretching bands, and the double-peak in the stretching band in the isotropic spectrum. By selectively freezing either the stretching or bending mode, we demonstrate that the peak in the intermediate region (2000–2400 cm⁻¹) of the isotropic spectrum arises from the interplay of the stretching and bending motions, while a substantial part of the peak in the same intermediate region of the anisotropic spectrum may be attributed to the combined motion of the bending and librational modes.

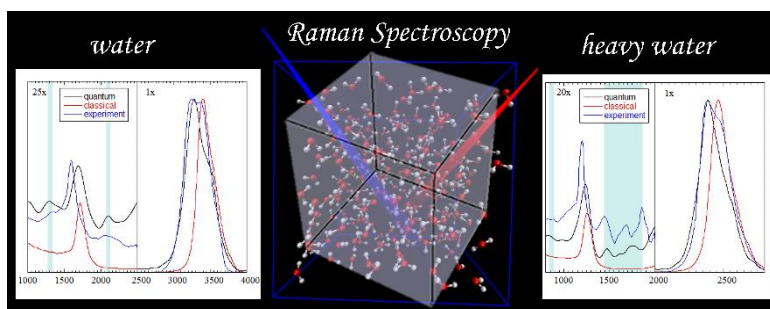


Fig. 1 The isotropic Raman spectrum of liquid water and heavy water at 298.15 K using the POLI2VS model.

Keywords: Raman spectroscopy, quantum dynamics, nuclear quantum effect

Reference

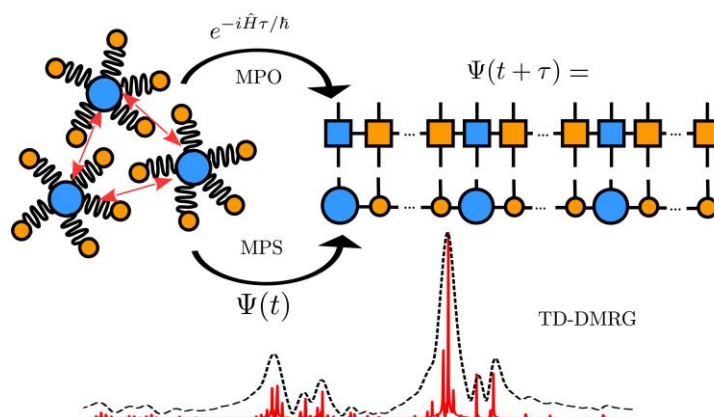
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Time Dependent Density Matrix Renormalization Group Algorithms for Nearly Exact Absorption and Fluorescence Spectra of Molecular Aggregates at Both Zero and Finite Temperature

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We implement and apply time-dependent density matrix renormalization group (TD-DMRG) algorithms at zero and finite temperature to compute the linear absorption and fluorescence spectra of molecular aggregates. Our implementation is within a matrix product state/operator framework with an explicit treatment of the excitonic and vibrational degrees of freedom, and uses the locality of the Hamiltonian in the zero-exciton space to improve the efficiency and accuracy of the calculations. We demonstrate the power of the method by calculations on several molecular aggregate models, comparing our results against those from multi-layer multiconfiguration time-dependent Hartree and n-particle approximations. We find that TD-DMRG provides an accurate and efficient route to calculate the spectrum of molecular aggregates. We also combine TD-DMRG and time-dependent Hartree (TDH) together to include the effects of the large sets of weakly coupled vibrations.



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Two unified thermostat schemes for efficient configurational sampling for classical/quantum canonical ensembles via molecular dynamics

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Molecular dynamics (MD) has been a useful tool for investigating and predicting properties in chemistry, physics, biology, materials science, etc. Dealing with canonical ensemble, various thermostats have been developed^[1-3]. We present two unified second-order integration schemes^[4-7] for constructing simple, robust and accurate algorithms for typical thermostats for configurational sampling for the canonical ensemble. The schemes are easy to be implemented into popular molecular dynamics modeling software, e.g. AMBER.^[8] Employing the algorithms developed from the schemes, accuracy may be increased by an order of magnitude for estimating coordinate-dependent properties in molecular dynamics (when the same time interval is used), irrespective of which type of thermostat is applied. The schemes are especially useful for path integral molecular dynamics (PIMD)^[4, 9], because they consistently improve the efficiency for evaluating all thermodynamic properties for any type of thermostat.

Keywords: canonical ensemble; “middle” scheme; configurational sampling

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