Stochastic Formalism and Simulations of Quantum Dissipative Dynamics

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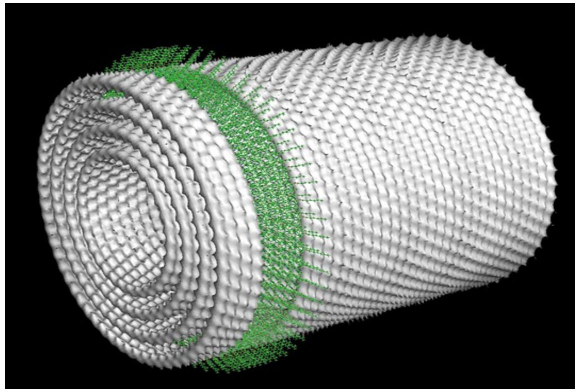
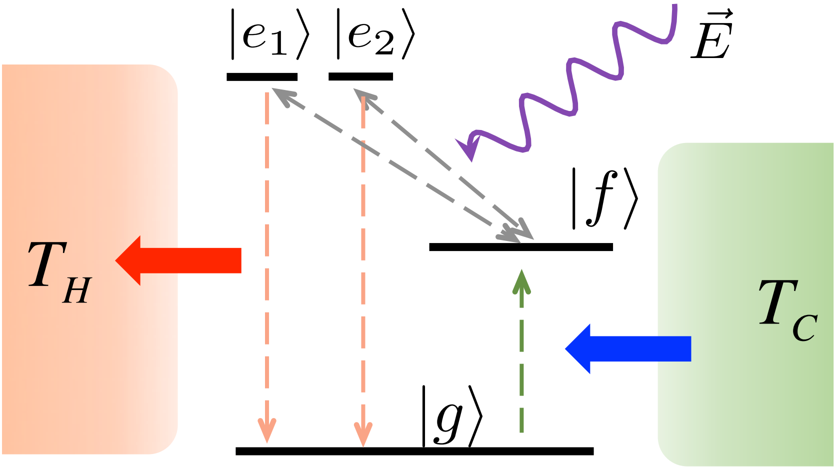
- Unified Stochastic Formalism (Chang-yu Hsieh)
- Stochastic Path Integral Simulations (Jeremy Moix)

Sept. 21, 2016, Ban Honnef, Germany
'Simulating quantum processes and devices'

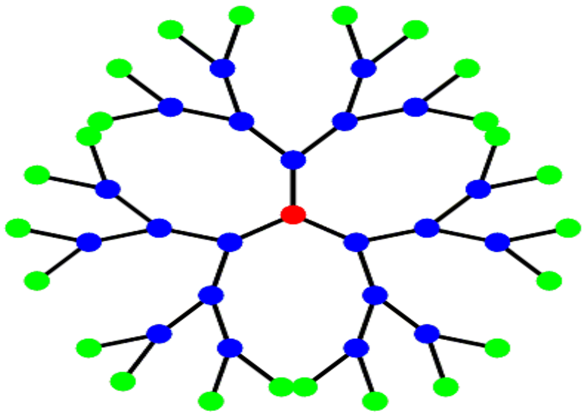
Applications to Quantum Processes



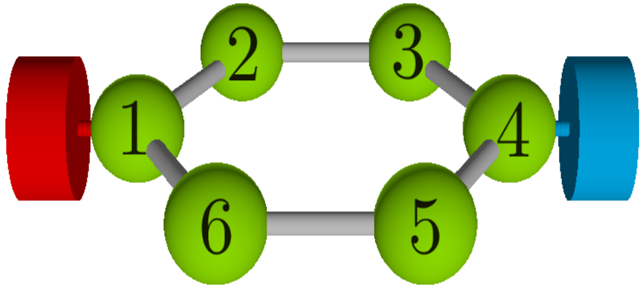
Quantum transport, PRL 116, 196803 (2016)



Quantum heat engines (pumps) NJP 18, p 023003 (2016)



Light-harvesting energy transfer PRL 110, 200402 (2013)



Heat transfer in Benzene Sci. Rep. 6, 28027 (2016)

Brownian Motion

Deterministic probability approach: Fokker-Planck Equation (1905)

$$\frac{\partial}{\partial t}P(x,t) = \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[D(x,t)P(x,t)\right].$$

Ensemble averaging: $A(t)= \langle A(x)\rangle_{P(t)}$

Stochastic trajectory approach: Langevin Equation of Motion (1908)

$$m\frac{d^2\mathbf{x}}{dt^2} = -\eta\frac{d\mathbf{x}}{dt} + \boldsymbol{f}(t).$$

Fluctuation-dissipation relation: $$\langle f_i(t) f_j(t')\rangle = 2\eta_{i,j}k_B T\delta(t-t').$$

Stochastic averaging: $A(t)= \langle A[f(t)]\rangle_{f(t)}$

Dissipative Quantum Dynamics

Deterministic probability approach:

$$\frac{\partial \rho(t)}{\partial t} = -i\mathcal{L}\rho(t)$$

Ensemble averaging: $A(t) = \langle A(x) \rangle_{\rho(t)}$

DMRG, HEOM, MCTDH, PIMC, QUAPI, Semi-classical, etc.

Stochastic trajectory approach:

$$\frac{\partial \psi(t)}{\partial t} = -i[\hat{H} + f(t)\hat{V}]\psi(t)$$

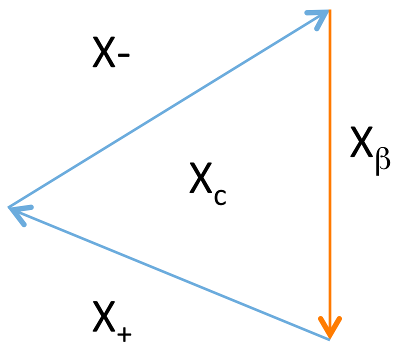
Fluctuation-dissipation relation: $\langle f(t) f(t') \rangle = C(t)$

Stochastic averaging: $A(t) = \langle A[f(t)] \rangle_{f(t)}$

Quantum state diffusion, Stochastic Liouville equation, Stochastic path integral, etc

A Novel Method for Simulating Quantum Dissipative Systems

J. Cao, L. W. Ungar, and G. A. Voth, J. Chem. Phys. 104, 4189 (1996)



1 Monte Carlo sampling of the Gaussian functional

$$\exp(-S_{bath}[x_c(t)])$$

2. Propagation of the system wave-function

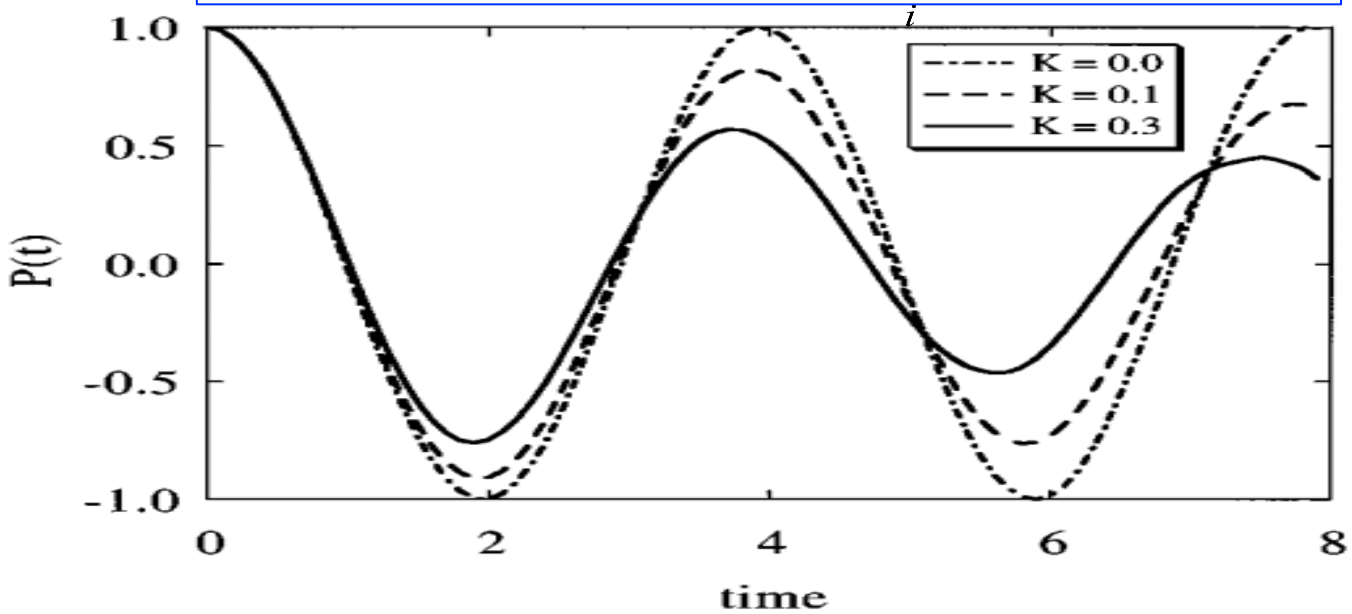
$$i\frac{\partial\psi}{\partial t} = [H_s + V(x_c(t), q)]\psi$$

3. Average of the bath configurations

spin-boson model

Kondo constant:

$$J(\omega) = \frac{\pi\hbar K}{2}\omega e^{-\omega/\omega_c}$$



Stochastic Wave-function for Gaussian Bath

Replace bath with stochastic force if V = f(x) A(q)

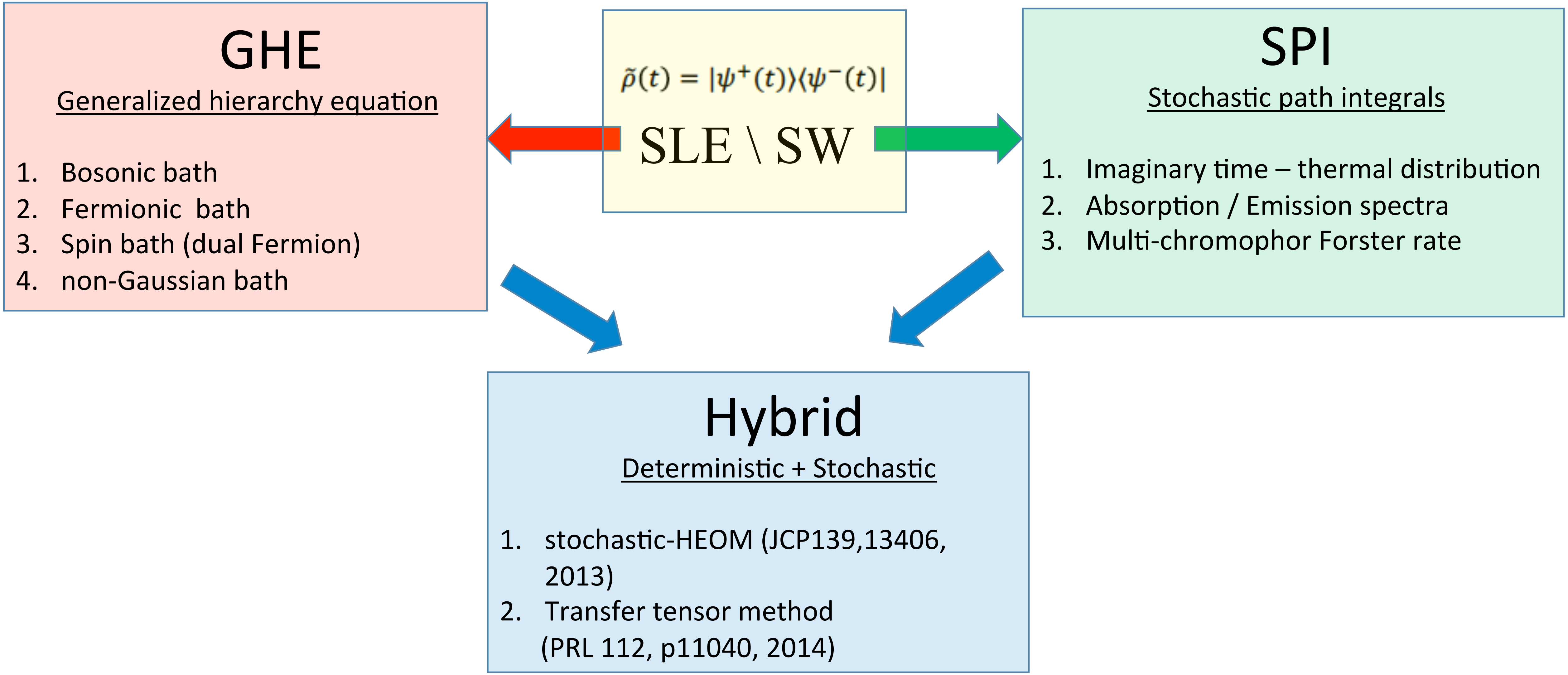
$$\begin{cases} i\frac{d}{dt}|\psi^-(t)\rangle = [H_s + f^{-*}(t)A]|\psi^-(t)\rangle \\ i\frac{d}{dt}|\psi^+(t)\rangle = [H_s + f^{+}(t)A]|\psi^+(t)\rangle \end{cases}$$

stochastic RDM $\tilde{\rho}(t) = |\psi^+(t)\rangle\langle\psi^-(t)|$

$$\frac{d\,\tilde{\rho}_s(t)}{dt} = -i[H_s, \tilde{\rho}_s] - iA\tilde{\rho}_s(t)f^+(t) + i\tilde{\rho}_s(t)Af^-(t)$$

Stockburger and Grabert, Phys. Rev. Lett., 88:170407, 2002

Goal: Generalize this equation to any bath models


GHE
Generalized hierarchy equation
1. Bosonic bath
2. Fermionic bath
3. Spin bath (dual Fermion)
4. non-Gaussian bath
$\tilde{\rho}(t) = |\psi^{+}(t)\rangle\langle\psi^{-}(t)|$
SLE \ SW
SPI
Stochastic path integrals
1. Imaginary time – thermal distribution
2. Absorption / Emission spectra
3. Multi-chromophor Forster rate
Hybrid
Deterministic + Stochastic
1. stochastic-HEOM (JCP139,13406, 2013)
2. Transfer tensor method (PRL 112, p11040, 2014)

System + Bath Quantum Dynamics

$$H = H_s + H_b + \mathrm{AB}$$

$$\rho(0) = \rho_s(0) \otimes \rho_b^{eq}$$

$$\frac{d\rho(t)}{dt} = -i[H, \rho(t)]$$

Three classes of bath models :

$$H_b = \sum_k \omega_k a_k^+ a_k \qquad [a_k, a_j^+] = \delta_{k,j}$$

Bosons

$$H_b = \sum_k \omega_k c_k^+ c_k \qquad \{c_k, c_j^+\} = \delta_{k,j}$$

Fermions

$$H_b = \sum_k \frac{1}{2} \sigma_k^z \qquad [\sigma_k^x, \sigma_k^y] = i\sigma_k^z$$

Spins

Stochastically Decoupled Quantum Dynamics

$$\frac{d\rho(t)}{dt} = -i[H, \rho(t)]$$

$$d\tilde{\rho}_s(t) = -i\,dt[H_s, \tilde{\rho}_s(t)] - \frac{i}{\sqrt{2}} A\tilde{\rho}_s(t)\,dW + \frac{i}{\sqrt{2}} \tilde{\rho}_s(t) A\,dV$$

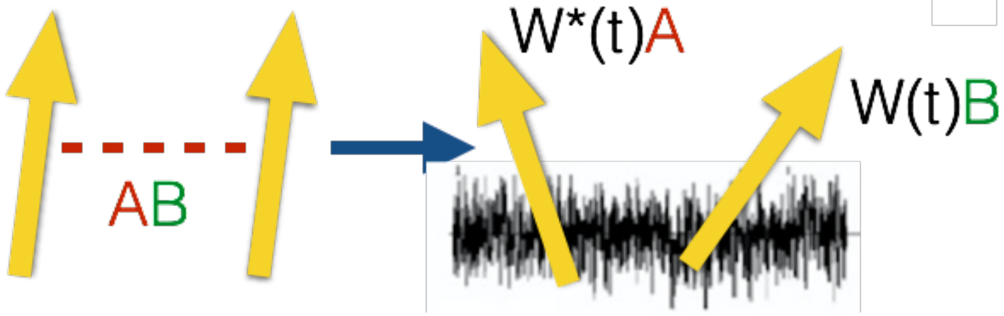
$$d\tilde{\rho}_b(t) = -i\,dt[H_b, \tilde{\rho}_b(t)] + \frac{1}{\sqrt{2}} dW^* B\tilde{\rho}_b(t) + \frac{1}{\sqrt{2}} dV^* \tilde{\rho}_b(t) B$$

White Noise Statistics $\overline{dW dW^*} = \overline{dV dV^*} = 2\,dt$

related work by J Shao

reduced density matrix

$$\rho_s(t) = \overline{\tilde{\rho}_s(t)\,\mathrm{Tr}_b\,\tilde{\rho}_b(t)}$$



encodes the bath-induced dissipations.

Bath-induced Dissipations and Multi-time Correlation Functions

$$d\tilde{\rho}_b(t) = -i\,dt\left[H_b, \tilde{\rho}_b(t)\right] + \frac{1}{\sqrt{2}} dW^* B\tilde{\rho}_b(t) + \frac{1}{\sqrt{2}} dV^* \tilde{\rho}_b(t) B$$

Take trace and obtain formal solution

$$\mathrm{Tr}_b \tilde{\rho}_b(t) = \exp\left(-\frac{1}{\sqrt{2}} \int_0^t (dW_s + dV_s) \mathcal{B}(s) \right)$$

Analogous to the influence functional.

forward / backward path
In terms of noise realization

The fluctuation and dissipation kernels as well as higher order responses encoded in bath's multi-time correlation functions.

Bath-induced fluctuating field

$$\mathcal{B}(t) = \mathrm{Tr}_b\left(B\,\tilde{\rho}_b(t)\right)$$

Bath-induced Dissipations and Multi-time Correlation Functions

$$\rho_s(t) = \overline{\tilde{\rho}_s(t)\,\mathrm{Tr}_b\,\tilde{\rho}_b(t)}$$

Bath-induced fluctuations

$$\mathrm{Tr}_b\tilde{\rho}_b(t) = \exp\left(-\frac{1}{\sqrt{2}}\int_0^t (dW_s + dV_s)\mathcal{B}(s)\right)$$

Analogous to the influence functional.

$$\mathcal{B}(t) = \frac{1}{\sqrt{2}}\int_0^t dW_s^*\Phi_{2,1}(t,s) + \frac{1}{\sqrt{2}}\int_0^t dV_s^*\Phi_{2,2}(t,s) +$$

$$+\left(\frac{1}{\sqrt{2}}\right)^3 \int_0^t\int_0^{s_1}\int_0^{s_2} dW_{s_1}^* dW_{s_2}^* dW_{s_3}^*\Phi_{4,1}(t,s_1,s_2,s_3) + \ldots +$$

$$+\left(\frac{1}{\sqrt{2}}\right)^3 \int_0^t\int_0^{s_1}\int_0^{s_2} dV_{s_1}^* dV_{s_2}^* dV_{s_3}^*\Phi_{4,8}(t,s_1,s_2,s_3) +$$

Only first two terms exist for Gaussian bath models.

Multi-time correlation functions convoluted with the noise histories.

Stochastic Liouville Equation (SLE)

A simple outline to obtain SLE, $\tilde{\rho}_s(t)\,\mathrm{Tr_b}\,\tilde{\rho}_b(t) \;\rightarrow\; \tilde{\rho}_s(t)$

$$\frac{d\,\tilde{\rho}_s(t)}{dt} = -i[H_s, \tilde{\rho}_s] \mp iA\tilde{\rho}_s\,(t)f^+(t) + i\tilde{\rho}_s\,(t)Af^-(t)$$

All distinguishing properties of various bath models are now hidden under the details of the noise: Complex-valued vs Grassmann-valued , Gaussian vs non-Gaussian etc.

Two-Time Statistics

$$\overline{f^+(t)f^+(t')} = C_{++}(t'-t)$$

$$\overline{f^+(t)f^-(t')} = C_{+-}(t'-t)$$

$$\overline{f^-(t)f^-(t')} = C_{--}(t'-t)$$

Bath's two-time correlation function (boson case)

$$C_{+-}(t) = \alpha_B(t) = \int d\omega J(\omega)\left(\coth\frac{\beta\omega}{2}\cos(\omega t) - i\sin(\omega t)\right)$$

Stockburger and Grabert, Phys. Rev. Lett., 88:170407, 2002

Stochastic Liouville Equation (SLE)

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$$\overline{f^-(t)f^-(t')} = C_{--}(t'-t)$$

Boson (complex-valued) vs Fermion (Grassmann-valued)

$$C_{++}(t'-t) = \begin{cases} \alpha_B(|t'-t|) & \text{Boson} \\ \theta(t-t')\alpha_F(t-t') - \theta(t'-t)\alpha_F(t'-t\quad) & \text{Fermion} \end{cases}$$

correlation functions with Bose-Einstein or Fermi-Dirac statistics.

Hsieh and Cao (to be submitted)

Stochastic Liouville Equation (SLE)

A simple outline to obtain SLE, $\tilde{\rho}_s(t)\,\mathrm{Tr_b}\,\tilde{\rho}_b(t) \rightarrow \tilde{\rho}_s(t)$

$$\frac{d\,\tilde{\rho}_s(t)}{dt} = -i[H_s, \tilde{\rho}_s] \mp iA\tilde{\rho}_s\,(t)f^+(t) + i\tilde{\rho}_s\,(t)Af^-(t)$$

All distinguishing properties of various bath models are now hidden under the details of the noise: Complex-valued vs Grassmann-valued , Gaussian vs non-Gaussian etc.

Two-Time Statistics

$$\overline{f^+(t)f^+(t')} = C_{++}(t'-t)$$

$$\overline{f^+(t)f^-(t')} = C_{+-}(t'-t)$$

$$\overline{f^-(t)f^-(t')} = C_{--}(t'-t)$$

Four-Time Statistics etc.

$$\overline{f^+(t_1)f^+(t_2)f^+(t_3)f^+(t_4)} = C_{++++}(t_2-t_1, t_3-t_2, t_4-t_1)$$

...

$$\overline{f^-(t_1)f^-(t_2)f^-(t_3)f^-(t_4)} = C_{----}(t_2-t_1, t_3-t_2, t_4-t_1)$$

Deterministic Solutions for SLE

1. Formal Averaging over Stochastic Variables

$$\frac{d\,\overline{\tilde{\rho}_S(t)}}{dt} = -i\left[H_S, \overline{\tilde{\rho}_S(t)}\right] \mp iA\overline{\tilde{\rho}_S\,(t) f^+(t)} \pm i\overline{\tilde{\rho}_S\,(t) f^-(t)}\,A$$

$$= -i\left[H_S, \overline{\tilde{\rho}_S(t)}\right] \mp iA\overline{\tilde{\rho}_S\,(t)\,\underline{\mathcal{B}(t)}} \pm i\overline{\tilde{\rho}_S\,(t)\underline{\mathcal{B}(t)}}\,A$$

2. Define Auxiliary Density Matrices (ADM), m = 0 is RDM

$$\rho^{[m]} = \overline{\tilde{\rho}_S\,\mathcal{B}^m(t)}$$

3. Deterministic Equations of Motions

$$d_t\left[\overline{\tilde{\rho}_s \mathcal{B}^m}\right] = \overline{d_t[\tilde{\rho}_s]\mathcal{B}^m} + \overline{\tilde{\rho}_s d_t \mathcal{B}^m} + \overline{d_t\tilde{\rho}_s d_t \mathcal{B}^m}.$$

From Stochastic to Hierarchical Equations

1. A suitable basis set: orthonormal function basis, exponential functions

$$C(t) = \sum_{j=1}^{K} \chi_j \phi_j(t) \qquad \int_0^T ds\, w(s)\phi_i(s)\phi_j(s) = \delta_{ij}$$

2. Decomposition of stochastic field B(t)

$$\mathcal{B}(t) = \sum_{j=1}^{K} \chi_j a_j(t). \qquad a_j(t) \equiv \left(\frac{1}{\sqrt{2}}\right) \int_0^t dU_s^* \phi_j(t-s),$$

3. Correspondingly a refined definition of auxiliary density matrices (ADM)

$$\bar{\rho}_{\boldsymbol{n}}(t) = \overline{\tilde{\rho}_S(t) a_1^{n_1}(t) \cdots a_K^{n_K}(t)}$$

n_j = 0,1,2,3… for bosons
n_j = 0 / 1 for fermions

Hsieh and Cao (to be submitted)

Hierarchy Equation for Boson Bath

$$\frac{d\bar{\rho}_{\mathbf{n}}}{dt} = -i\left[\hat{H}_{\mathbf{s}}, \bar{\rho}_{\mathbf{n}}\right] + i\sum_j \chi_j \left(A\bar{\rho}_{\mathbf{n}+\mathbf{1}_j} - \bar{\rho}_{\mathbf{n}+\mathbf{1}_j}A\right)$$
$$+i\sum_j \phi_j(0)\left(A\bar{\rho}_{\mathbf{n}-\mathbf{1}_j} + \bar{\rho}_{\mathbf{n}-\mathbf{1}_j}A\right)$$
$$+\sum_{j,j'} \eta_{jj'}\bar{\rho}_{\mathbf{n}_{j\to j'}},$$

exponential decay: HEOM (Tanimura)
extended-HEOM (Wu)
quantum phase transition in sub-ohmic spin-boson model (Ankerhold)

Hierarchy Equation for Fermions

$$\frac{d\bar{\rho}_{\mathbf{n}}}{dt} = -i\left[\hat{H}_s, \bar{\rho}_{\mathbf{n}}\right] + i\sum_j \chi_j \left(A\bar{\rho}_{\mathbf{n}+\mathbf{1}_j} + \bar{\rho}_{\mathbf{n}+\mathbf{1}_j}A\right)\underline{(-1)^{|\mathbf{n}|_j}(1-n_j)}$$
$$+i\sum_j \phi_j(0)\left(A\bar{\rho}_{\mathbf{n}-\mathbf{1}_j} + \bar{\rho}_{\mathbf{n}-\mathbf{1}_j}A\right)\underline{(-1)^{|\mathbf{n}|_j}n_j}$$
$$+\sum_{j,j'} \eta_{jj'}\bar{\rho}_{\mathbf{n}_{j\to j'}}\underline{(-1)^{|\mathbf{n}|_j+|\mathbf{n}|_{j'}}n_j(1-n_{j'})},$$

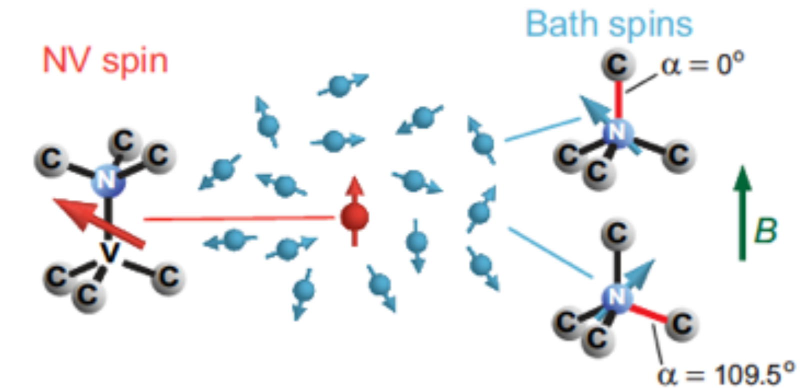
Pauli exclusion and negative sign due to anti-commutativity

finite-tiers for Fermions
correlation functions beyond exponential forms
application: dual fermion representation of spins

Related work on Fermion bath: Strunz, Yan, etc.

Spin-Based Quantum Devices

Nitrogen-Vacancy Spins in Diamond

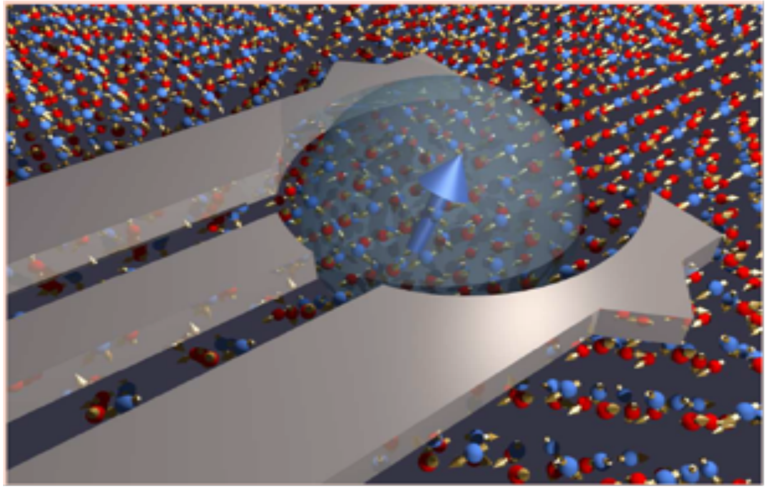


Applications:

quantum computing and room-temperature ultra-precision magnetic sensors.

Source of Spin Noises:
$1/r^3$ dipolar coupling to 10^1~10^2 impurity spins.

Spin-Based Qubit in Gated QM Dots



Coish et. al.

Source of Spin Noises:

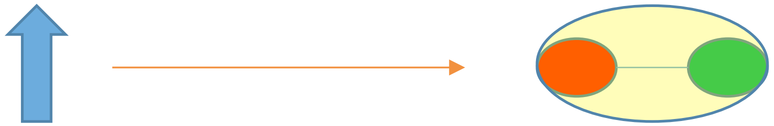
Hyperfine coupling and 10^4~10^6 nuclear spins

Casting Spin Bath as Fermionic Bath
Dual Fermion Representation

$$\sigma_k^x \Rightarrow \left(c_k^{+} - c_k\right)\left(d_k^{+} + d_k\right) \qquad \sigma_k^y \Rightarrow -i\left(c_k^{+} + c_k\right)\left(d_k^{+} + d_k\right) \qquad \sigma_k^z \Rightarrow -2\left(c_k^{+} c_k - \frac{1}{2}\right)$$

C-fermion: Jordan-Wigner Transformation. Represent spin algebra with fermions

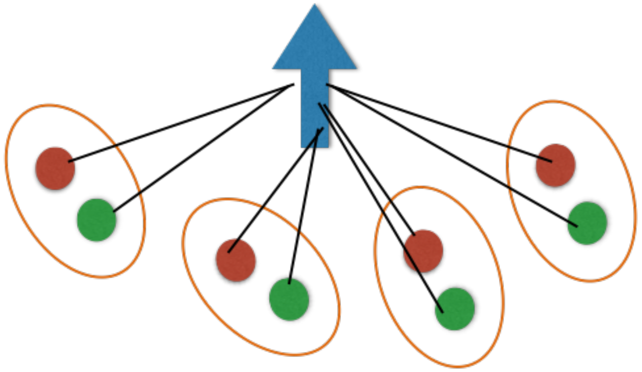
D-fermion: Correct the minus sign of fermion representations for multiple spins.



The Effective Two-Bath Model

$$H = H_s + \sum_k \frac{\omega_k}{2} \sigma_k^z + \sigma_0^z \sum_k g_k \sigma_k^x$$

Dual-Fermion Mapping



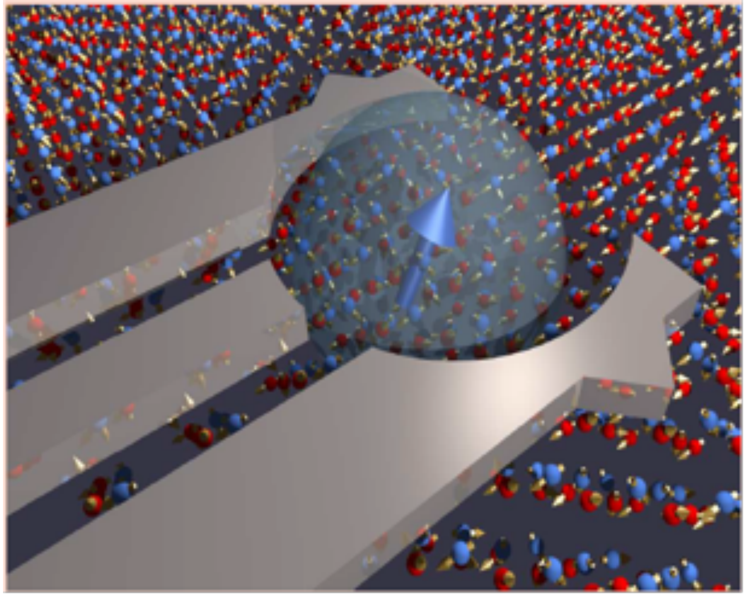
$$H = H_s + \sum_k \omega_k \left(c_k^+ c_k - \frac{1}{2} \right) + i\sigma_0^z \sum_k g_k (c_k^+ + c_k)(d_k^+ + d_k)$$

General Strategy:

1. Stochastically decouple C-Fermions and derive SLE for D-Fermions and Central spins.
2. Trace out the D-Fermions in SLE.
3. Formally average out the C-Fermions to obtain the spin equation.

Spin Bath: Fermionic Mapping

$$H = \frac{\omega_0}{2}\sigma_0^z + \sum_{k>0} \frac{\omega_k}{2}\sigma_k^z + \sigma_0^z \sum_{k>0} g_k \sigma_k^x$$



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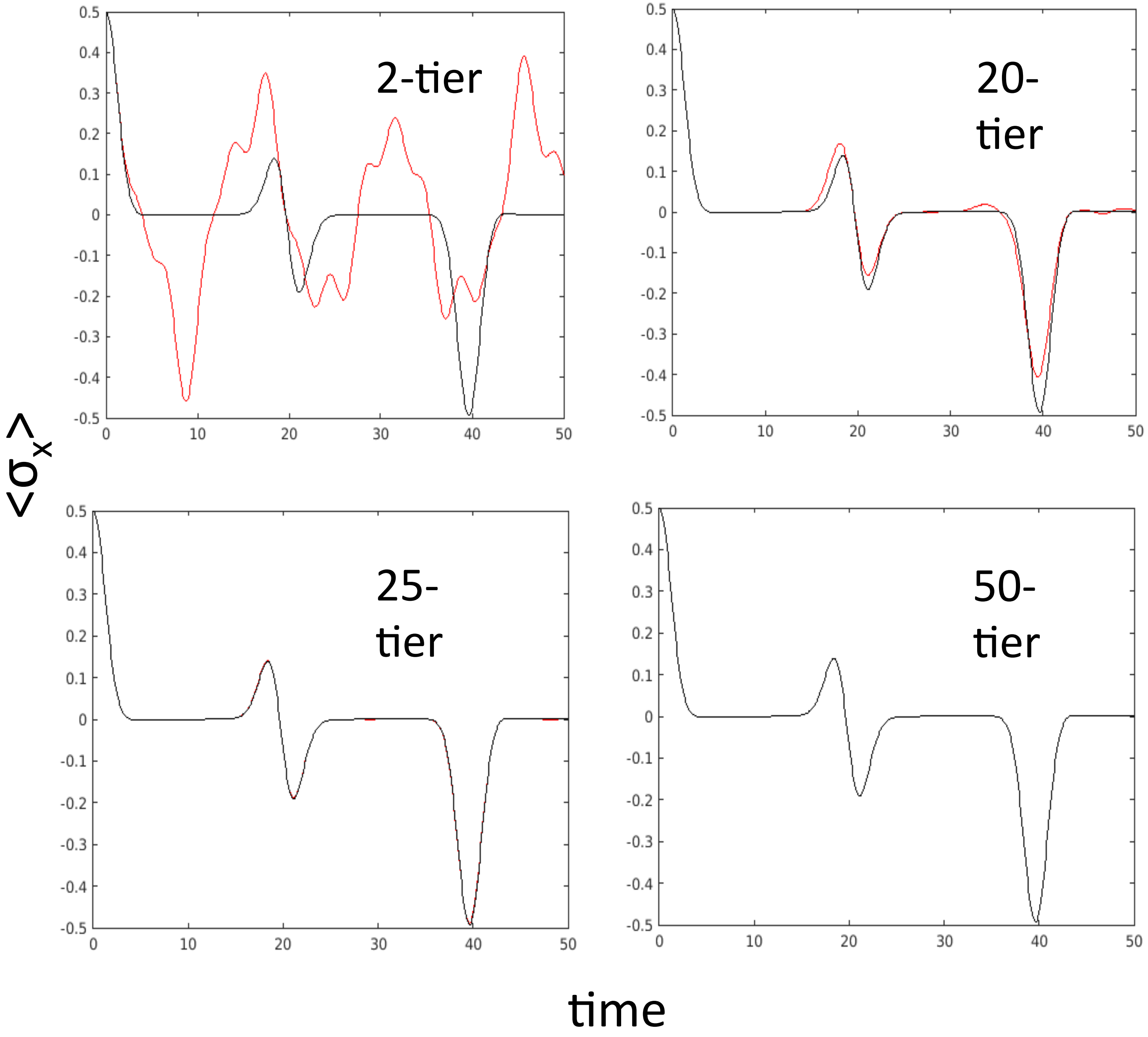
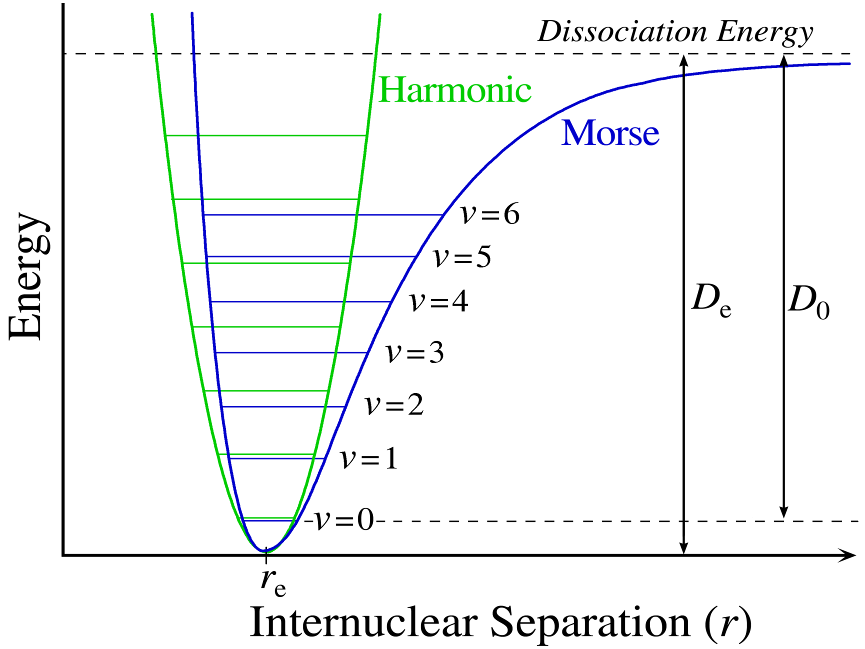


Condensed Phased Dynamics:
Spin Bath as an Anharmonic Environment

anharmonic bath model

$$H = \frac{\epsilon}{2}\sigma_z + \Delta\sigma_x + \sum_{k>0}\left(\frac{1}{2}P_k^2 + D_k(1-e^{-\alpha_k X_k})^2\right)$$
$$+\sigma_z \sum_{k>0} g_k X_k$$

Effective spin bath when only 2 bound states in each bath oscillator.



spin bath model

$$H = \frac{\epsilon}{2}\sigma_z + \Delta\sigma_x + \sum_{k>0}\frac{\Omega_k}{2}\sigma_k^z + \sigma_z\sum_{k>0}\tilde{g}_k\sigma_k^x$$

$$E_{v,k} = \omega_k\left(v+\frac{1}{2}\right) - \frac{\alpha_k^2}{2}\left(v+\frac{1}{2}\right)^2$$

Generalized Hierarchy Equation (GHE) : Anharmonic Bath

$$\partial_t \rho^{[\mathbf{A}_1][\mathbf{A}_2][\mathbf{A}_3]\cdots} = -i\left[H_s, \rho^{[\mathbf{A}_1][\mathbf{A}_2][\mathbf{A}_3]\cdots}\right] - i\sum_{n,m,\boldsymbol{j}} \chi_{\boldsymbol{j}}^{n+1,m}\left[A, \rho^{\cdots[\mathbf{A}_n+(m,\boldsymbol{j})]\cdots}\right]$$

$$-i\sum_{n,m,\mathbf{j}} \phi_{j_1}(0) A \rho^{\cdots[\mathbf{A}_{n-1}+(m',\boldsymbol{j}_1)][\mathbf{A}_n-(m,\boldsymbol{j})]\cdots} - i\sum_{n,m,\mathbf{j}} \phi_{j_1}(0) \rho^{\cdots[\mathbf{A}_{n-1}+(m',\boldsymbol{j}_1)][\mathbf{A}_n-(m,\boldsymbol{j})]\cdots} A$$

$$+\sum_{n,m,\mathbf{jj}'} \eta_{\mathbf{jj}'} \rho^{\cdots\left[a^n_{m\mathbf{j}} \to a^n_{m\mathbf{j}'}\right]\cdots}$$

(3-layers of hierarchy)

1. $[A_N]$ Block matrix accounts for the (N+1)-th cumulant expansion of the influence functional. In case of Gaussian bath, only $[A_1]$ contains non-zero elements.

2. N-th order cumulant contributions only emerge at (N-1)-th tier with closed system dynamics at zero-th tier.

3. When dealing with the Gaussian bath, the present approach reduces to the extended Hierarchical Equations of motions.

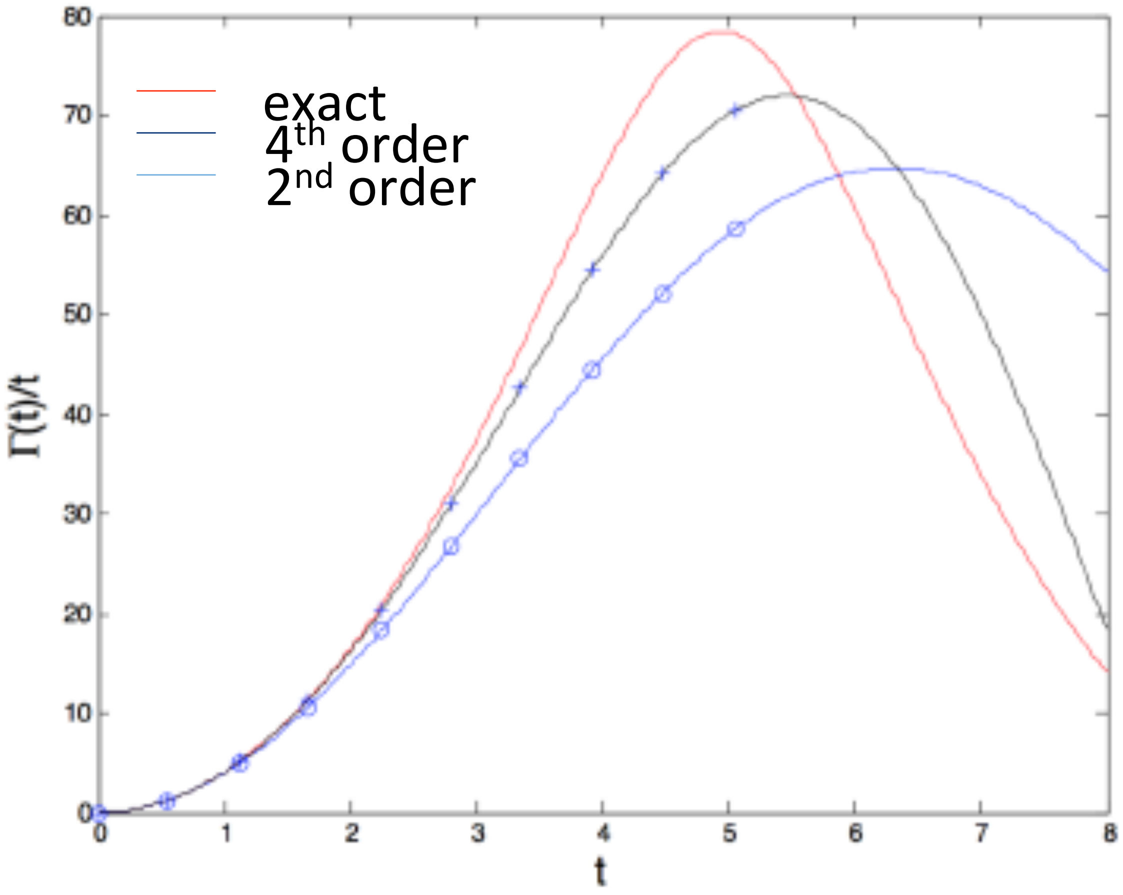
Spin Bath: 4-th Order Corrections

$$H = \frac{\omega_0}{2}\sigma_0^z + \sum_{k>0}\frac{\omega_k}{2}\sigma_k^z + \sigma_0^z \sum_{k>0} g_k \sigma_k^x$$

$$\langle\uparrow|\,\rho_s\,|\downarrow\rangle\,(t) = \langle\uparrow|\,\rho_s\,|\downarrow\rangle\,(0)e^{-i\epsilon t}e^{\Gamma(t)}$$

$$\Gamma(t) = \sum_k \ln\left[1 - \frac{4g_k^2}{\Omega_k^2}\left(1-\cos\Omega_k t\right)\right]$$

$$\Omega_k = \omega_k\sqrt{1+(4g_k^2/\omega_k^2)}.$$



Summary

Paper I

The family of hierarchy equations provides a numerically exact description for generic quantum environments. Specifically, we derived hierarchy equations for Grassmann noise and non-Gaussian noise from the stochastic Liouville Equation.

Paper II

Spin bath is treated in two different approaches. Physical spins (such as nuclear spins) should be treated in the dual-fermion approach and go deep down the hierarchical tiers. Spin bath (as anharmonic condensed environment) is more conveniently handled by generalized hierarchy equation (GHE) approach, which goes beyond the linear response and the Gaussian assumption.

GHE

Generalized hierarchy equation

1. Bosonic bath
2. Fermionic bath
3. Spin bath (dual Fermion)
4. non-Gaussian bath

SLE \ SW

$$\tilde{\rho}(t) = |\psi^{+}(t)\rangle\langle\psi^{-}(t)|$$

SPI

Stochastic path integrals

1. Imaginary time – thermal distribution
2. Absorption / Emission spectra
3. Multi-chromophor Forster rate

Hybrid

Deterministic + Stochastic

1. stochastic-HEOM (JCP139,13406, 2013)
2. Transfer tensor method
   (PRL 112, p11040, 2014)

Reduced Density Matrix (RDM)

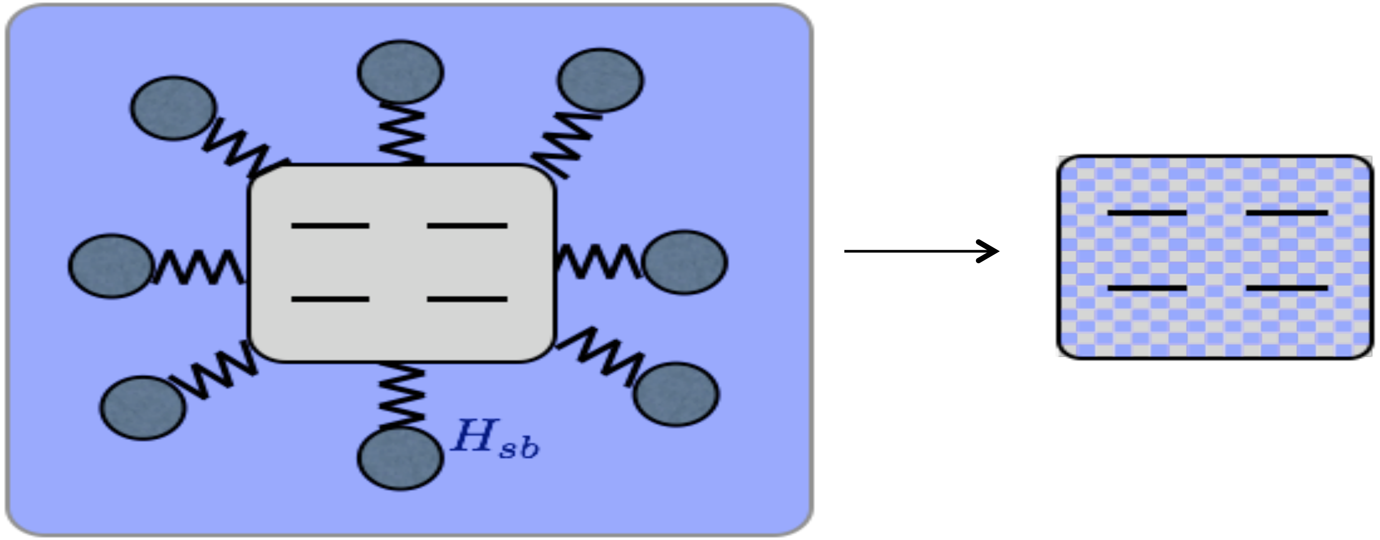
System-bath Hamiltonian: $$H = H_s + H_b + H_{sb}$$

canonical distribution: weak coupling to an equilibrium thermal bath

Goal: equilibrium RDM

$$\rho(\beta) = \frac{1}{Z}\mathrm{Tr_b} e^{-\beta H}$$
$$\neq \frac{1}{Z_s} e^{-\beta H_s}$$

(H_s and H_{sb} do not commute)



RDM is a non-canonical distribution function (i.e. not Boltzmann of the system)

Imaginary-time Path Integral

Integrating the bath:

$$\rho(x_s', x_s; \hbar\beta) = \frac{1}{Z}\int \mathcal{D}[q_s] e^{-\frac{1}{\hbar}\left(S_s^E[q_s] - \Phi[q_s]\right)}$$

Richard Feynman

Feynman-Vernon influence functional:

$$\Phi[q] = \int_0^{\hbar\beta} d\tau \int_0^{\tau} dt' q(\tau) K(\tau - \tau') q(\tau')$$

Imaginary-time correlation function:

$$K(\tau) = \int_0^{\infty} \frac{d\omega}{\pi} J(\omega) \frac{\cosh(\hbar\beta\omega/2 - \omega\tau)}{\sinh(\hbar\beta\omega/2)}$$

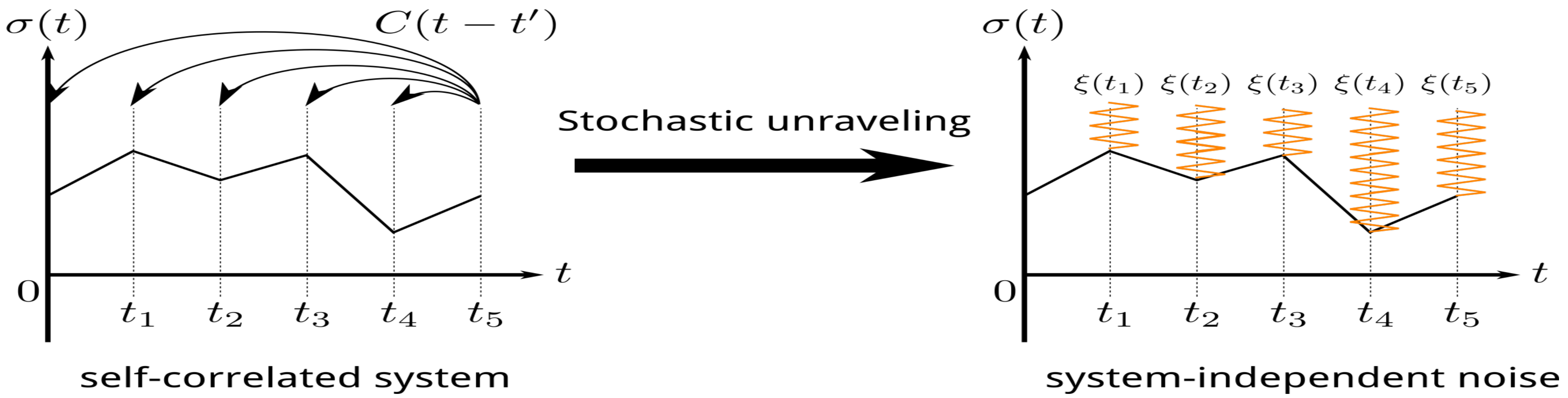
Bath spectral density:

$$J(\omega) = \frac{\pi}{2}\sum_j \frac{c_j^2}{\omega_j}\delta(\omega - \omega_j)$$

The time non-local correlation is difficult to evaluate, so we use the Hubbard-Stratonovich transformation to de-convolute the non-local influence functional

Feynman and Vernon, Ann. Phys. 24, 118, 1963

Stochastic Path Integral



Stochastic Schrodinger Equation (equivalent to GLE):

$$\frac{d}{d\tau}\rho(t) = -H(\tau)\rho(\tau)$$

$$\hat{H}(\tau) = \hat{H}_s + \xi(\tau)\hat{q}$$

correlation function for quantum noise:

$$\langle \xi(\tau)\xi(\tau')\rangle = K(\tau-\tau')/\hbar$$

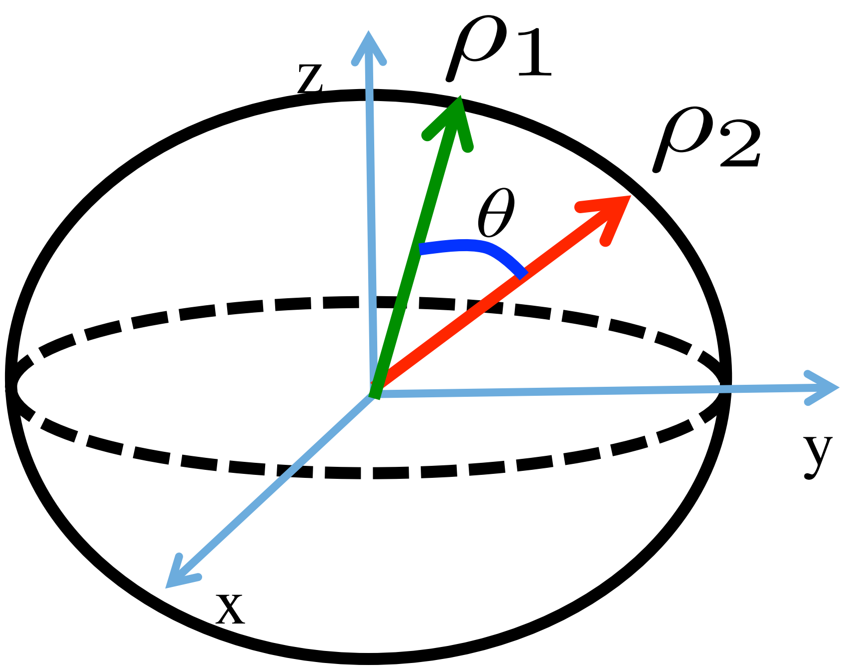
Advantages

- Numerically exact
- Arbitrary spectral densities
- Wave-function propagation

programs available for download

Moix, Zhao, and Cao, PRB, 85, 115412, (2012)

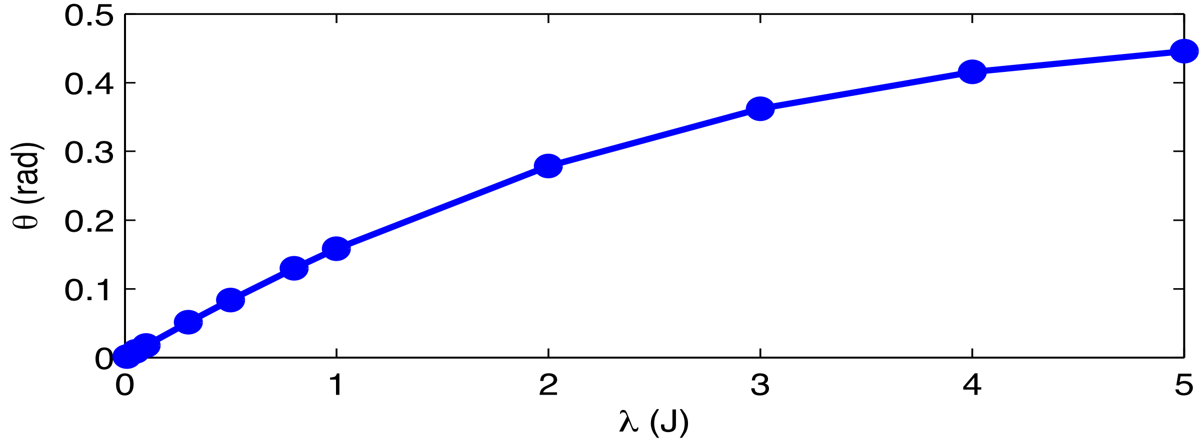
Basis Set Rotations

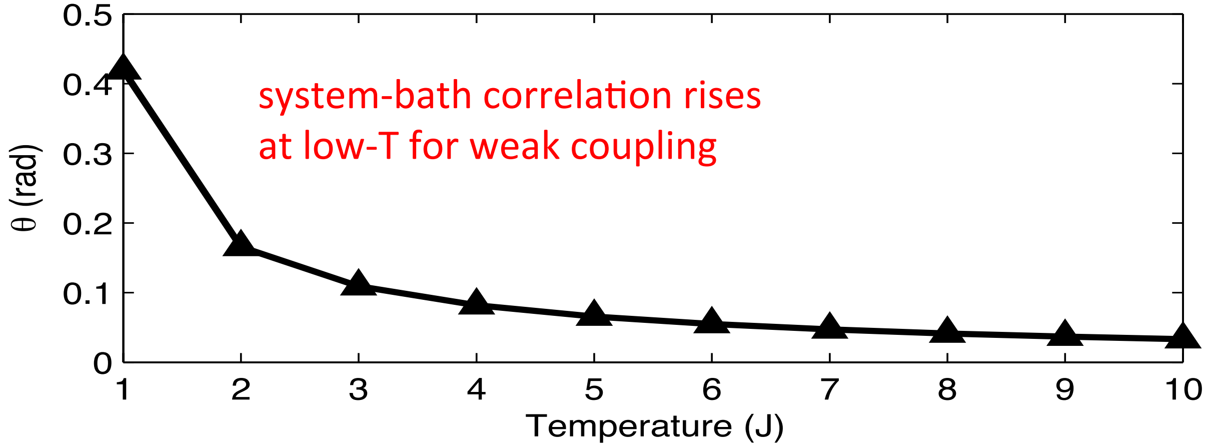


$$H_s = \Delta\sigma_z + J\sigma_x$$

$$\Delta = J$$

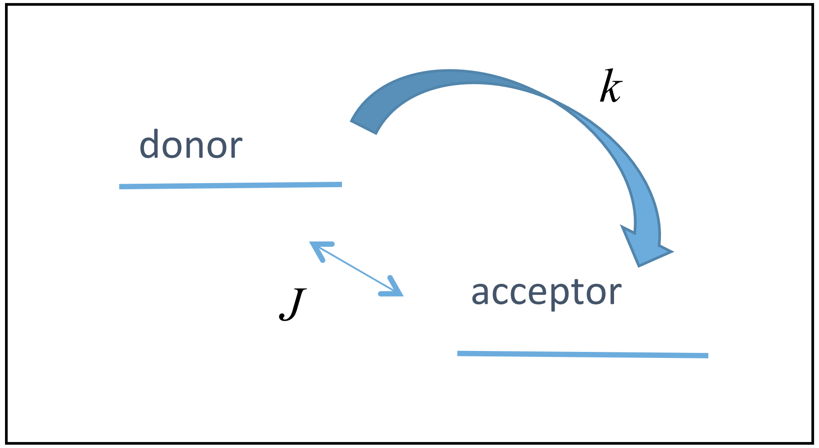
$$\omega_c = 5J$$

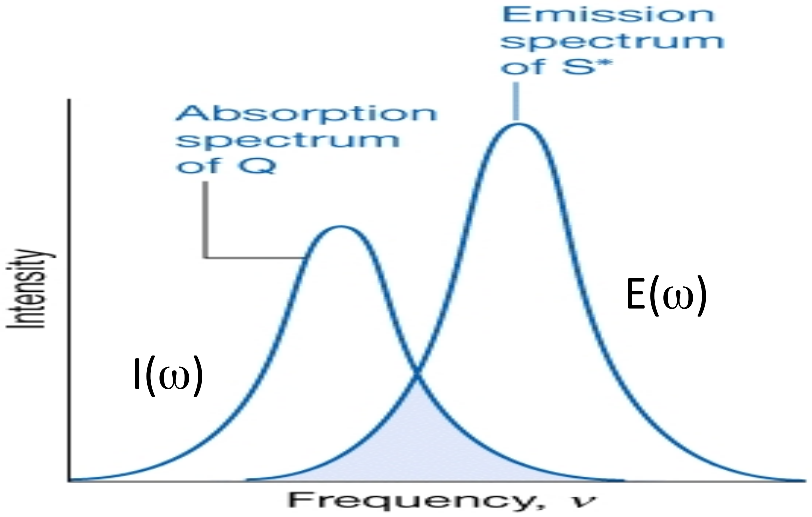




Lee, Cao, and Gong, PRE, 86, 021109, (2012); Cerrillo and Cao, PRL 112, p110401 (2014)

Förster Energy Transfer Theory



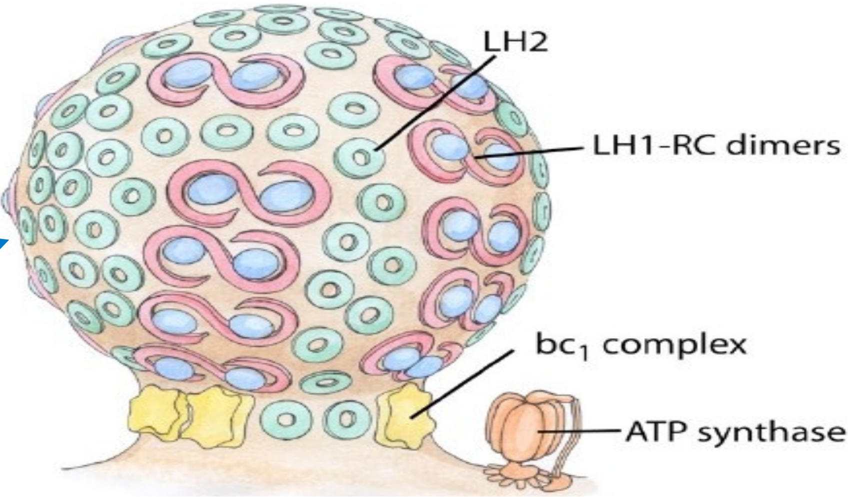


$$\text{rate} \propto |J|^2 \int_0^{\infty} d\omega I(\omega) E(\omega)$$

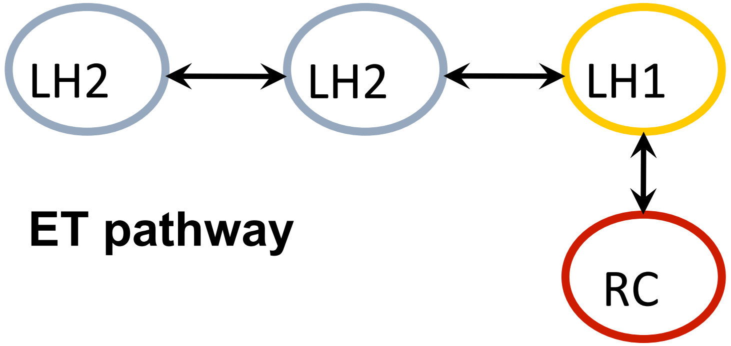
dipole coupling ($1/R^6$) overlap of emission and absorption spectra

Forster theory works at far field and fails at near field

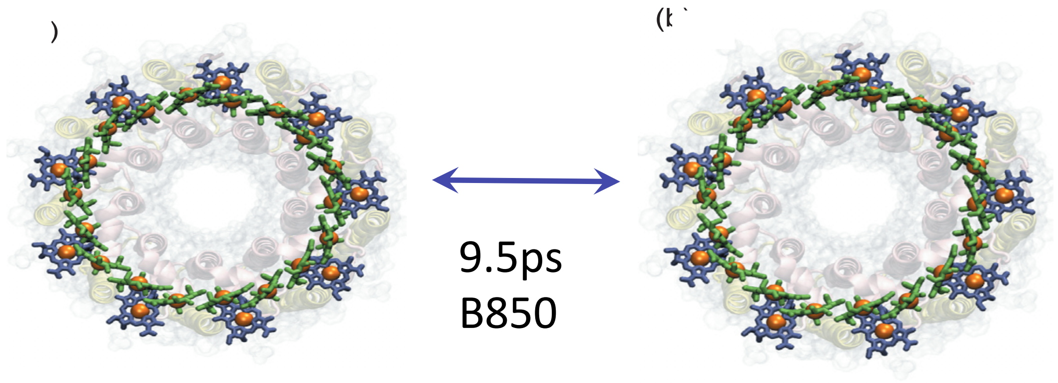
Photosynthetic Membranes of Purple Bacteria

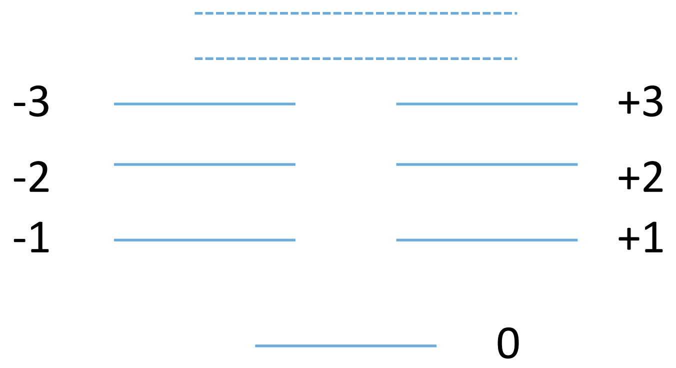


LH2 domains



ET pathway

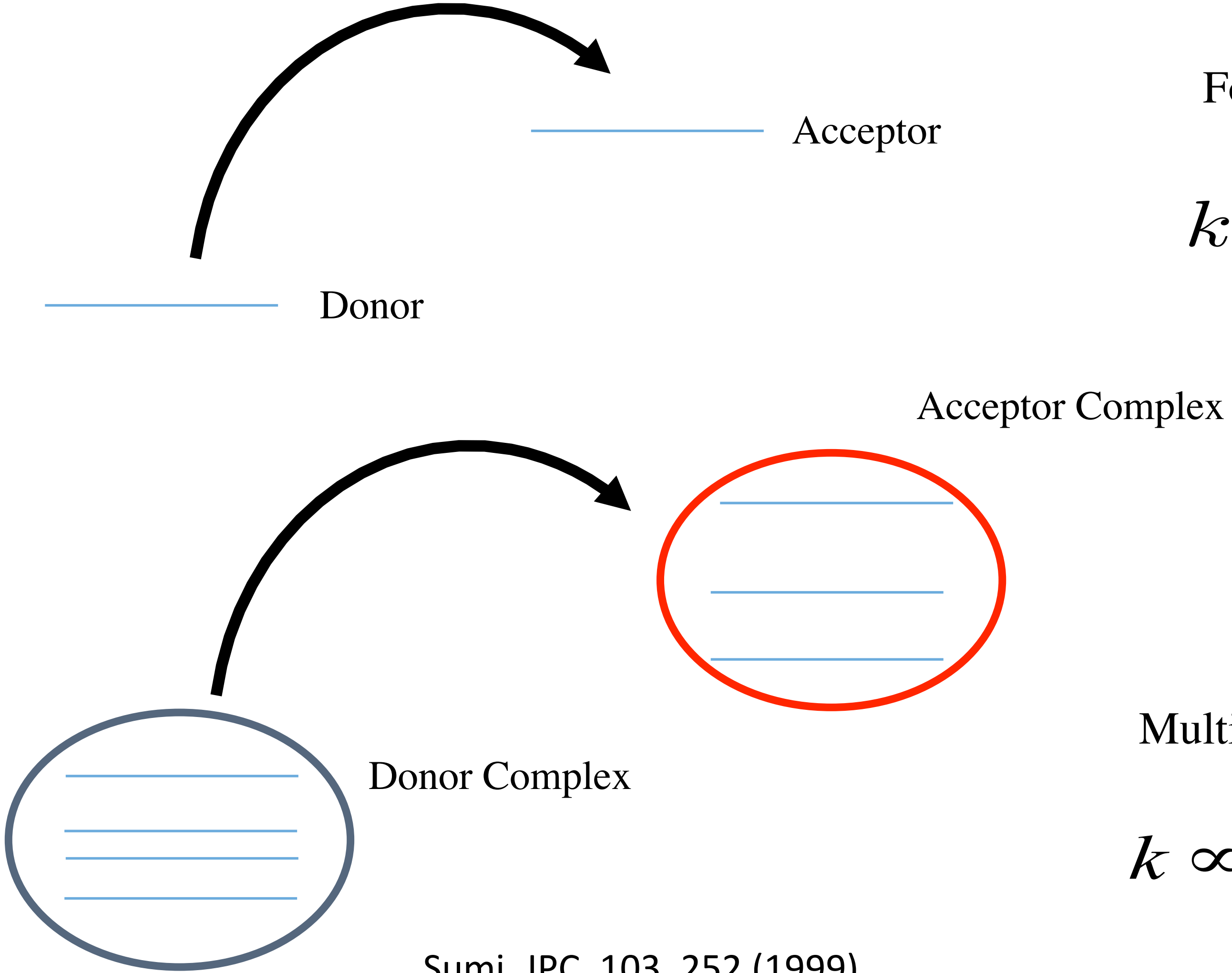




9-fold symmetry enhances transfer ⟷ The lowest state is dark

Dipole selection rule suggests no transfer from the lowest state of LH2 B850

Generalized FRET rates



Sumi, JPC, 103, 252 (1999)

Forster rate between molecules:

$$k \propto J^2 \int d\omega I^{\mathrm{A}}(\omega) E^{\mathrm{D}}(\omega)$$

$$\mathrm{Tr}(\hat{E}^D) = E^D$$
$$\mathrm{Tr}(\hat{I}^A) = I^A$$

Multi-chromophoric Forster rate:

$$k \propto \int Tr[\hat{J}^{AD}\hat{E}^{D}(\omega)\hat{J}^{DA}\hat{I}^{A}(\omega)]d\omega$$

the dipole selection rule breaks down at near field so the dark state transfers

System-bath Correlations in Emission

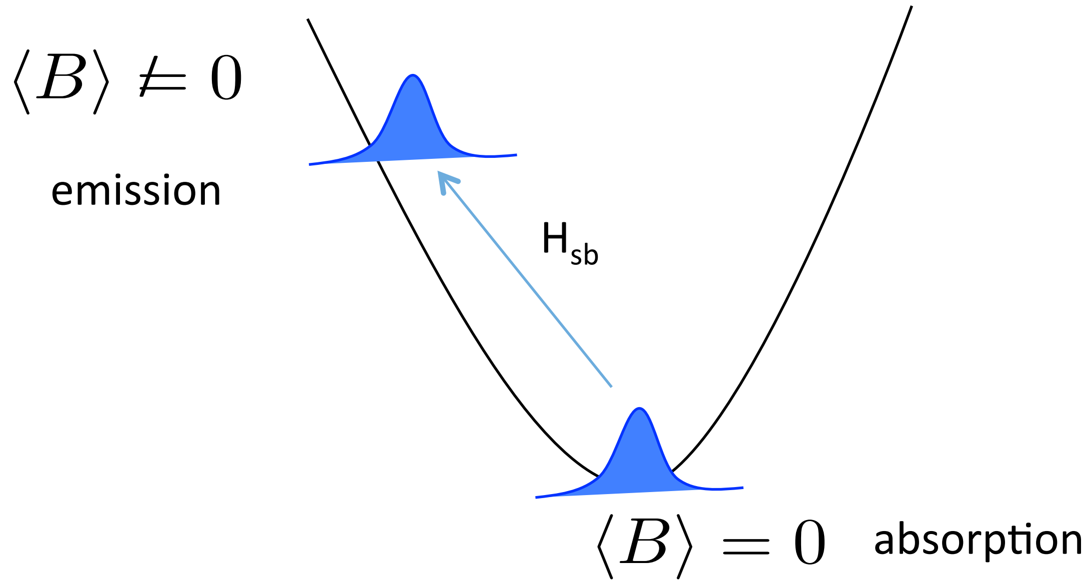
Why does the second-order work for absorption but fail for emission?

$$\rho^{\mathrm{A}} = I_{\mathrm{s}} \otimes \rho_b$$

Product state for absorption

$$\rho^{\mathrm{D}} = e^{-\beta H^{\mathrm{D}}} / Z^{\mathrm{D}}$$

Entangled state of the *entire* system and bath
(emission from dark state)



Standard 2rd-order perturbation does not properly describe system-bath correlations

Ma, Moix, and Cao, JCP 142, p094108; p094107; p094106 (2015)

Absorption and Emission

Acceptor's Absorption Operator:

$$I^{\mathrm{A}}(t) = \mathrm{Tr_b}\left[e^{-\frac{i}{\hbar}H^{\mathrm{A}}t}\rho^{\mathrm{A}}e^{+\frac{i}{\hbar}H_{\mathrm{b}}^{\mathrm{A}}t}\right]$$

$$\rho^{\mathrm{A}} = I_{\mathrm{s}} \otimes \rho_b$$

Product state

Donor's Emission Operator:

$$E^{\mathrm{D}}(t) = \mathrm{Tr_b}\left[e^{+\frac{i}{\hbar}H^{\mathrm{D}}t}\rho^{\mathrm{D}}e^{-\frac{i}{\hbar}H_{\mathrm{b}}^{\mathrm{D}}t}\right]$$

$$\rho^{\mathrm{D}} = e^{-\beta H^{\mathrm{D}}}/Z^{\mathrm{D}}$$

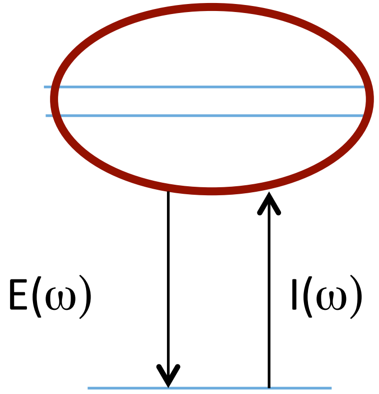
Entangled state of the *entire* system and bath

Detailed balance relations:

$$E(\omega) = \frac{e^{\hbar\beta\omega}}{Z}I(\omega)$$

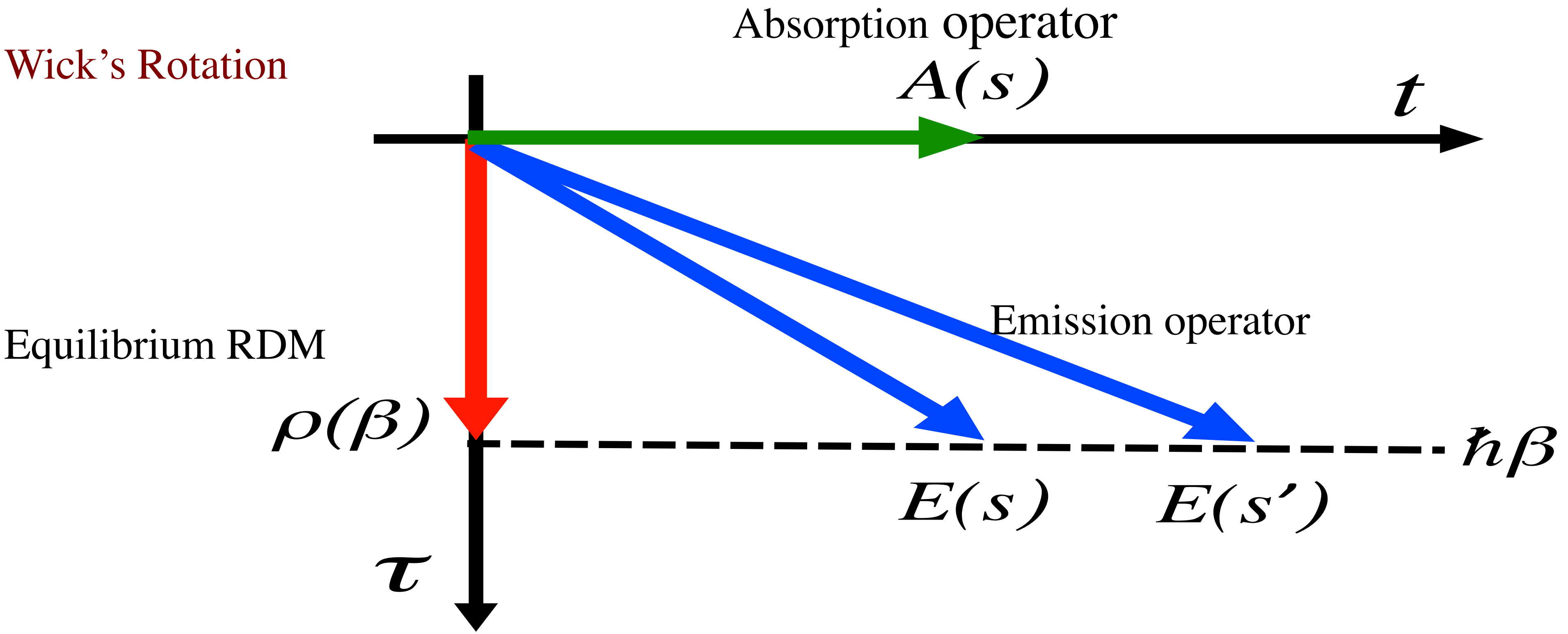
Emission is equivalent to absorption in complex time

$$E(t)^* = \frac{1}{Z}I(t - i\hbar\beta)$$



Ma and Cao, JCP 142, 094108

Integration Contours



Imaginary time:

$z = -i\tau$

reduced density matrix (RDM)

Real time:

$z = t$

absorption matrix

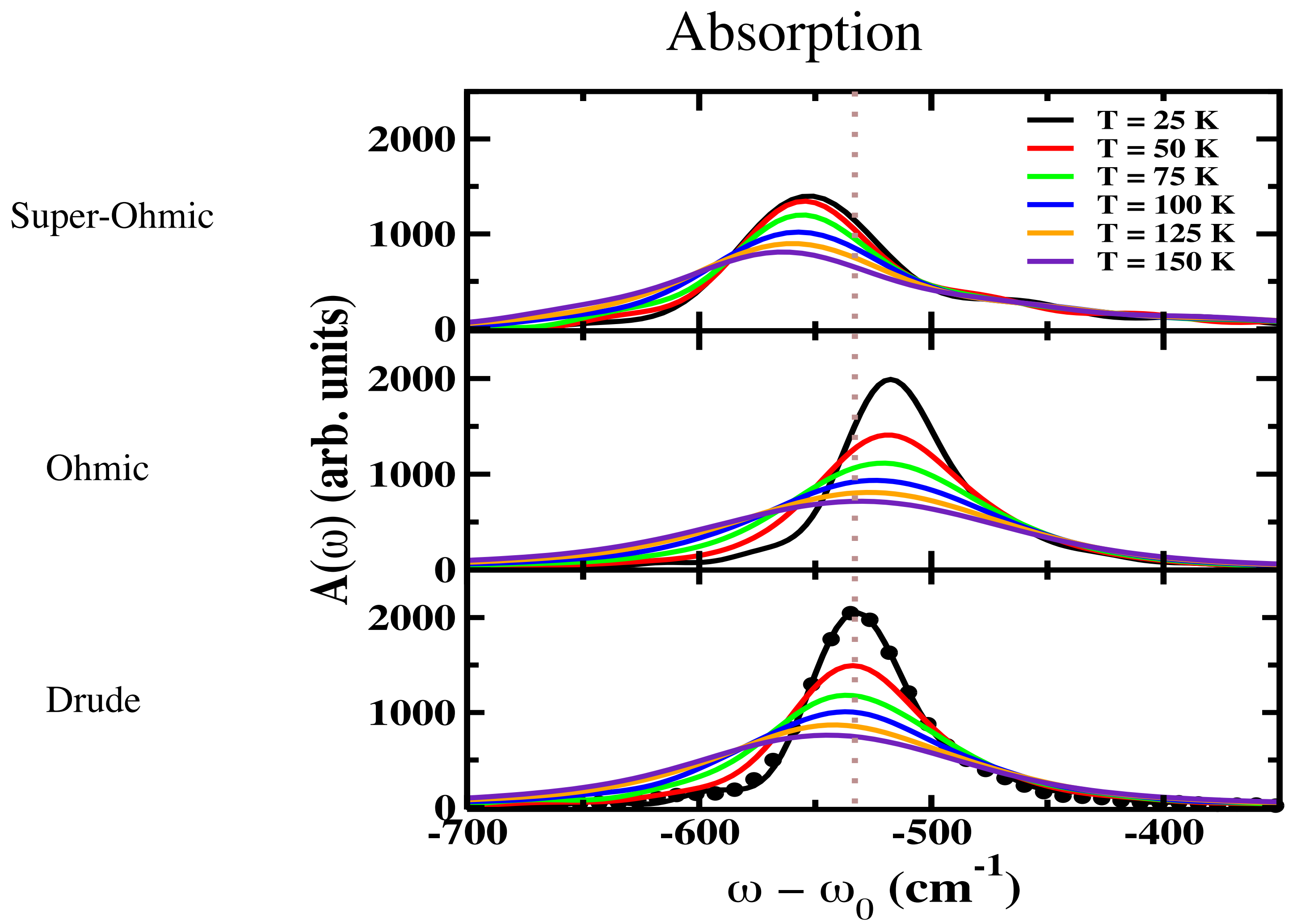
Complex time:

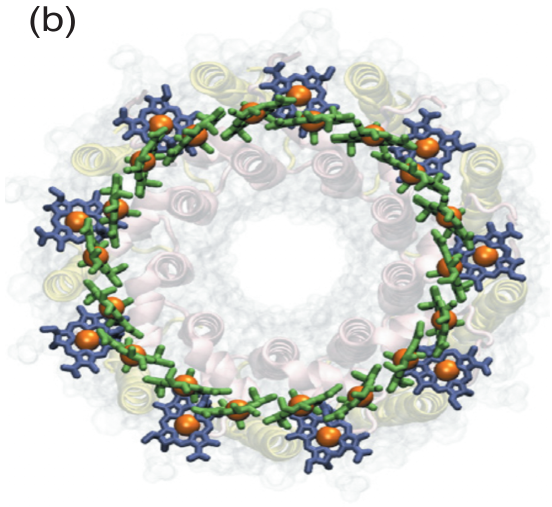
$z = t - i\tau$

emission matrix

Moix, Ma, Cao, JCP, 142 , 094108 (2015)

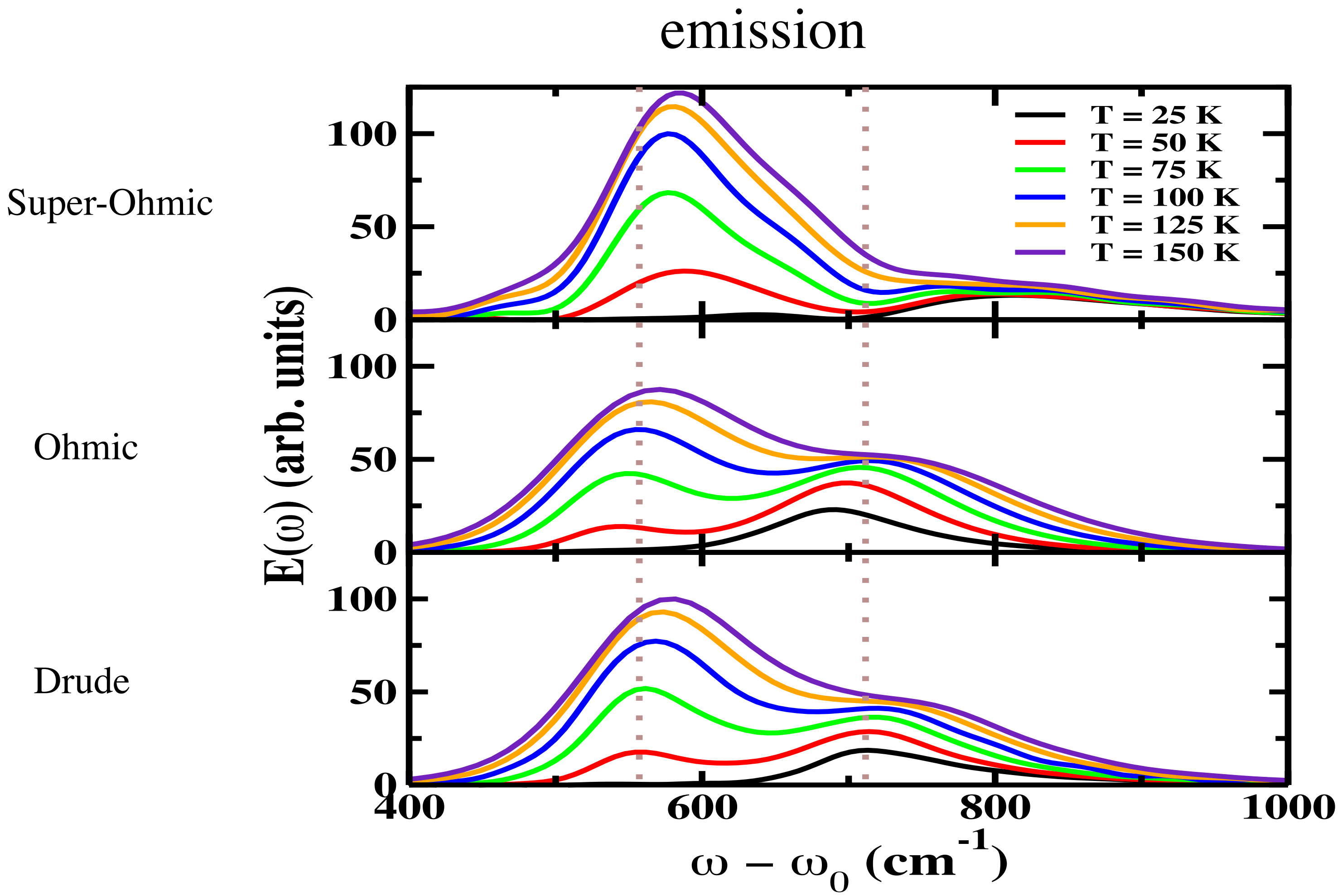
Example I: Spectra of LH2 B850

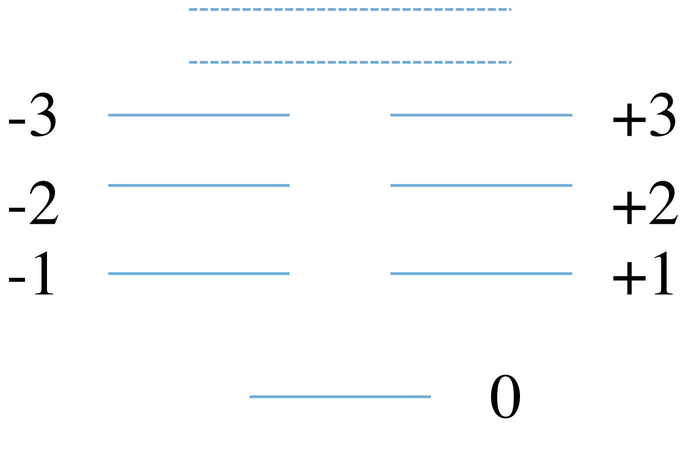




line-width increases with T, peak shift is sensitive to $J(\omega)$

Example II: Spectra of LH2 B850

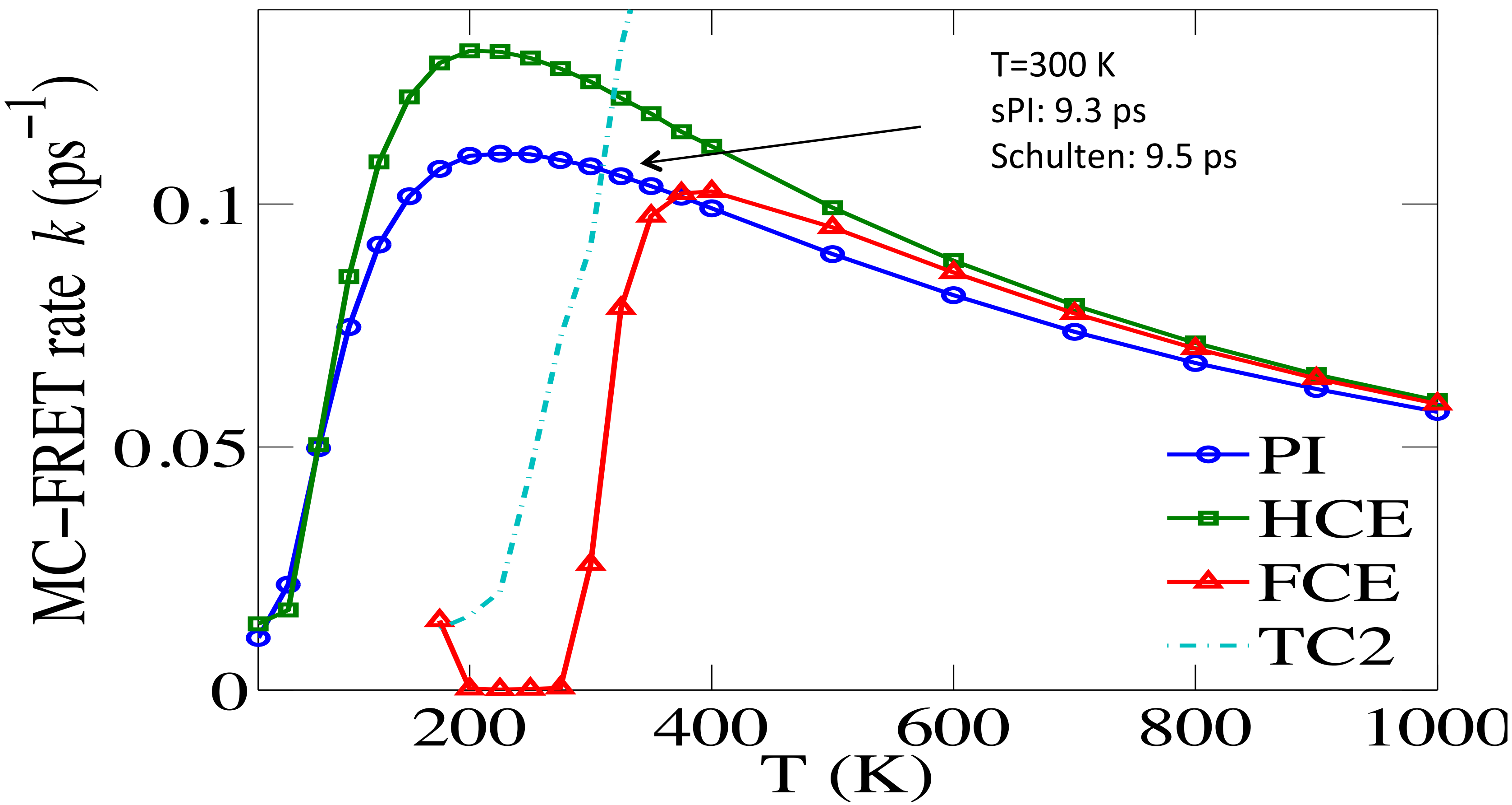


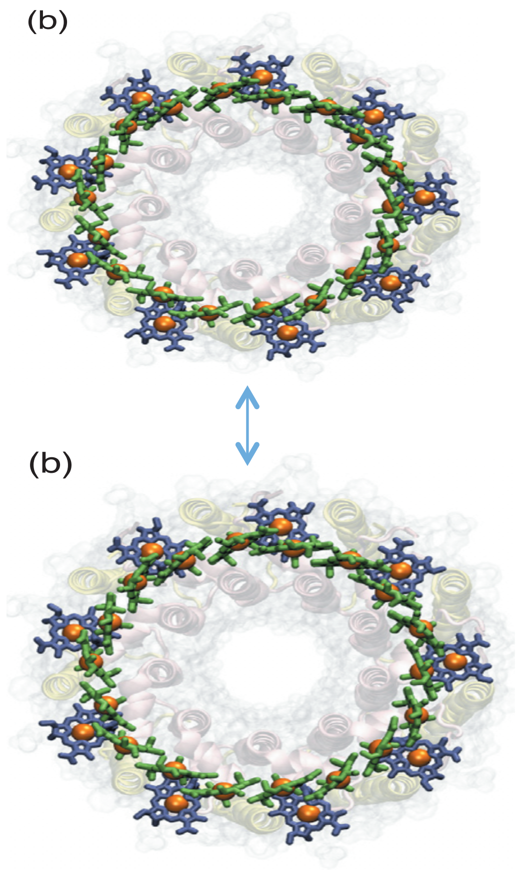


the lowest state is dark
k=+/-1 is bright state
(general for J-aggregates)

At low T, the bright state becomes dark because of exp(-βE), and k=0 becomes bright due to the LH-protein entanglement

Example III: LH2 MC-Forster Transfer rates





Transfer rate (with coherence): 9.3ps

Transfer rate (with disorder): 20ps

Cleary and Cao, NJP (2013) and Moix, Ma, Cao, JCP 142, 094108 (2015)

Conclusion

A family of hierarchy equations are obtained from the SLE.

Stochastic simulations are efficient and accurate for equilibrium and spectra calculations

Coworkers: Changyu Hsieh, Jeremy Moix, Javier Cerrillo

Funding: NSF and SMART

Thanks you for your attention!