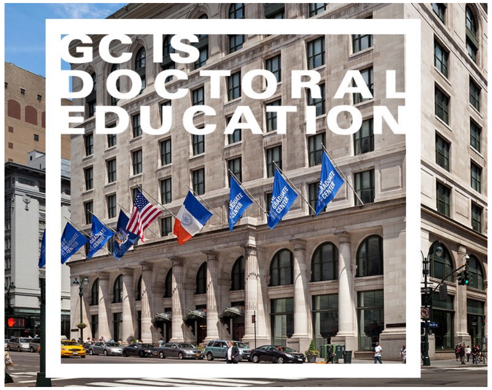
Open System Quantum Dynamics and Quantum Estimation

Seogjoo J. Jang

Queens College and the Graduate Center
City University of New York (CUNY) &
KIAS, KAIST (visiting)



THE GRADUATE CENTER
CITY UNIVERSITY OF NEW YORK

QUEENS COLLEGE

CU NY The City University of New York

Jang Group

Postdoc


Pablo Ramos

Fomer Postdocs


Ning Chen


Daniel Montemayor


Eva Rivera

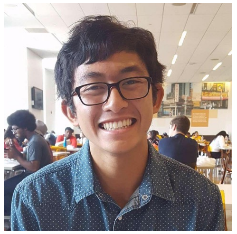

Praveen Kumar


Lei Yang

PhD student

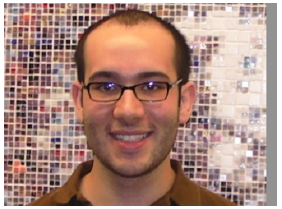

Taner Ture

Former PhD and Master's students


Ryan Pangilinan


Murali Devi


Marta Kowalczyk


Andres Montoya-Castilo

Collaborators

Youmg Min Rhee, Justin Caram, Chanbong Hyeon, A. Braunschweig, D. Eisele,
B. Mennucci, G. A. Voth, K.B. Whaley, G. R. Fleming, T. Berkelbach, D. R. Reichman, J. Eaves, Y.-C. Cheng,
Younjoon Jung, (the late) R. J. Silbey, Marshall D. Newton,…

Support

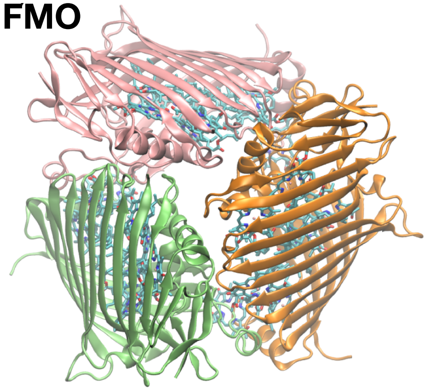
National Science Foundation, Department of Energy
KIAS, KAIST (KAIX)

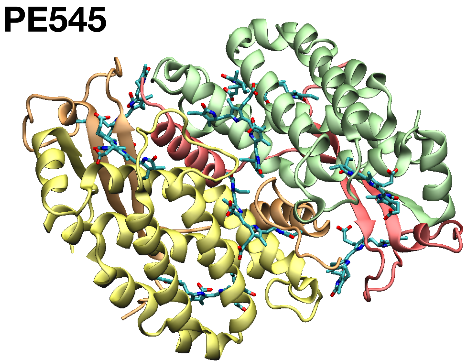
CCIS, Queens College, CUNY HPCC at Staten Island, CFN, Brookhaven National Lab.

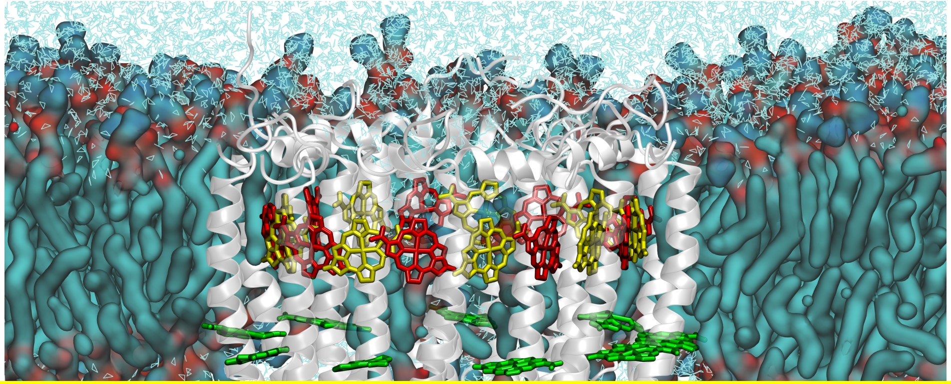
Three major natural light harvesting complexes

REVIEWS of
MODERN PHYSICS

July–September 2018
Volume 90, Number 3

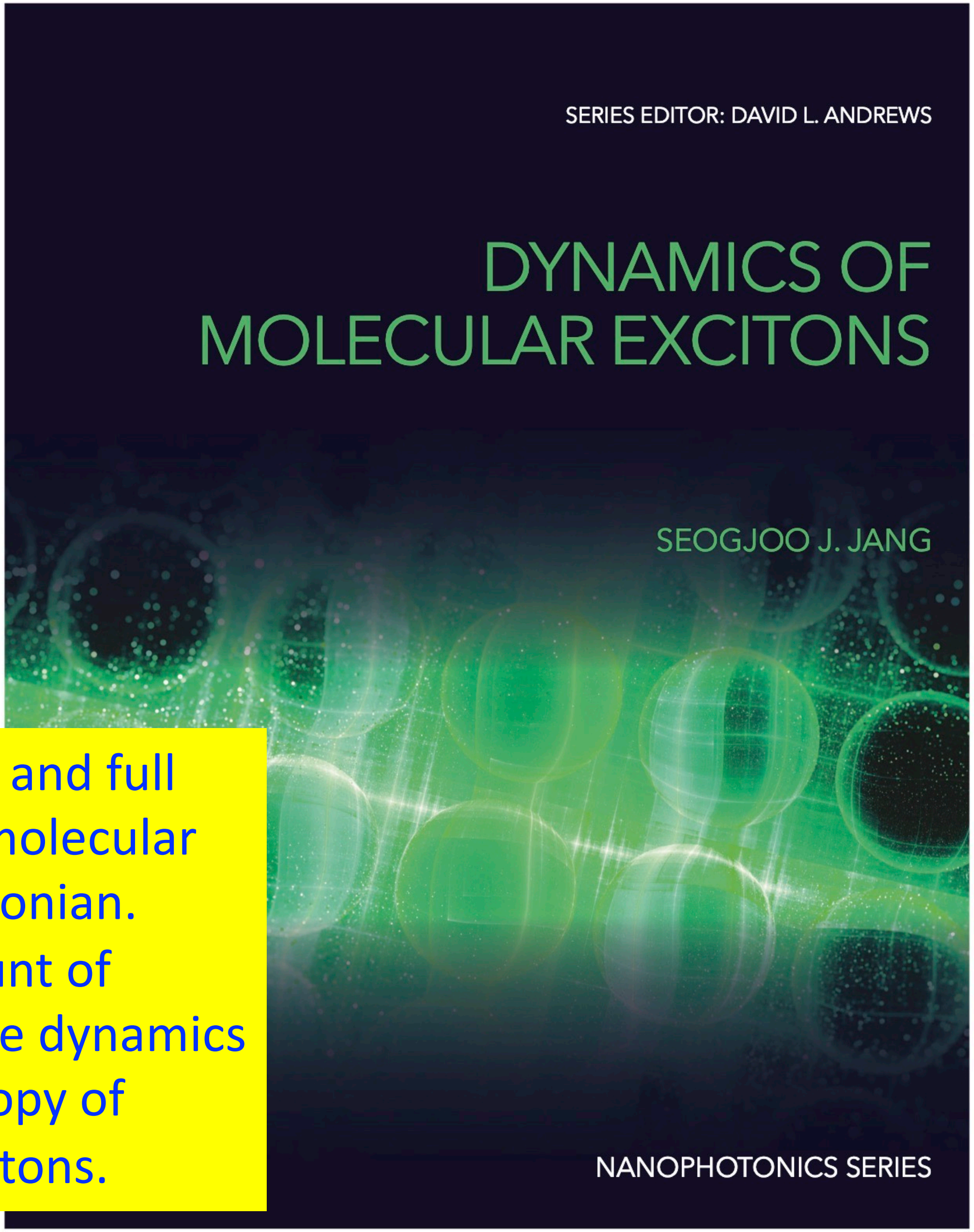






- Review of key experimental and theoretical results.
- Comprehensive description of all quantum mechanical principles and calculations.
- Identification of key design principles.

Jang and Mennucci, *Rev. Mod. Phys.* **90**, 035003 (2018)


SERIES EDITOR: DAVID L. ANDREWS

DYNAMICS OF
MOLECULAR EXCITONS

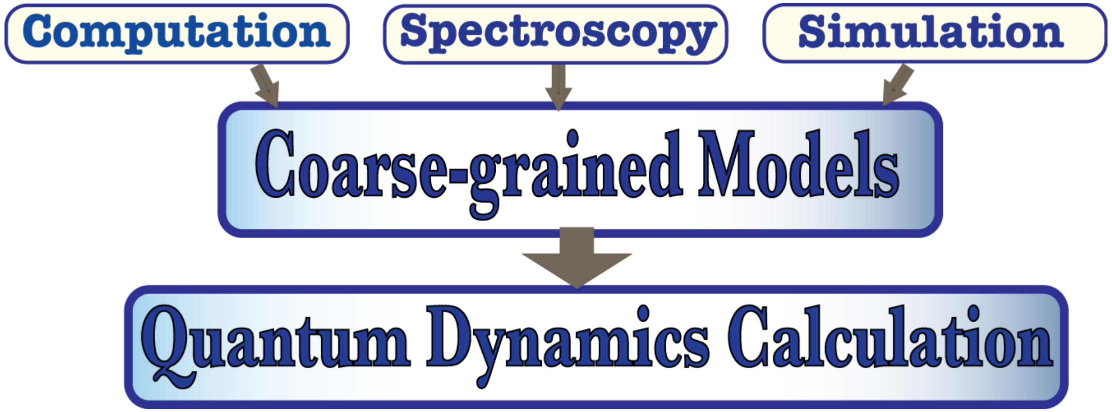
SEOGJOO J. JANG

NANOPHOTONICS SERIES

- Self-contained and full derivation of molecular exciton Hamiltonian.
- Detailed account of theories for the dynamics and spectroscopy of molecular excitons.

Jang, Dynamics of Molecular Excitons (Elsevier, 2020)

Quantum Dynamics and Kinetics in Condensed and Complex Environments



Computation

Spectroscopy

Simulation

Coarse-grained Models

Quantum Dynamics Calculation

- **Theory Development**: Energy transfer & Electron transfer
- **Method Development**: Path integral & Quantum Master equation

Long Term Objective: All-atomistic computational methods capable of providing quantitative description of quantum coherence, tunneling, nonlinearity, and anharmonicity.

New theories and computational demonstration of Chemical Sensing, Quantum Sensing & Information at molecular level

New Approaches for Machine Learning Interfacing Theories and Computational & Experimental Data

Outline of Talk

- Overview of open system quantum dynamics and quantum information & sensing
- Quantum estimation theory
- Quantum entropy production
- Issues with Markovian approximation in open system quantum dynamics
- Exact equations for open system quantum dynamics and recent advances
- Brief accounts of my own research on open system quantum dynamics

Open System Quantum Dynamics?

Description of the dynamics of a quantum system interacting with environments/reservoirs/baths of much larger (often assumed infinite dimensional) size.

- Nuclear magnetic resonance
- Quantum Optics
- Condensed Matter Physics
- Mathematical Physics & Astrophysics
- Quantum Computation, Information, Control, and Sensing
- Chemical and Biological Physics: Excited electronic and vibration dynamics of molecules or aggregates

- Quantum Master Equation (QME): Time evolution of a reduced density operator.
- Master Equation (ME): Time evolution of populations
- Quantum Fokker-Planck Equation (QFPE): Phase-space representation of QME, which approaches a Fokker-Planck Equation in the classical limit.
- Direct real time path integral calculation: Influence functional formalism

Quantum Computation: Potentials and Issues

- Quantum algorithms for classically intractable problems – factorization

- Complexity theory arguments – quantum states prepared by quantum computers have “super-classical properties,” eg. correlated probabilities

- Quantum computer of reasonable size cannot be simulated by any classical computer

- Measurement error for super-conducting Q-bits: 1% (Trapped ions are worse)

- Error correction requires much more qubits than actual qubits involved in calculation

John Preskill, “Quantum computing in the NISQ era and beyond,”
Quantum 2, 79 (2019)[arXiv:1801.00862v3]

Current Status of Quantum Information – Noisy Intermediate Scale Quantum Computing (NISQ) and Quantum Sensing

- Quantum computation in the near term – demonstration and confirmation of quantum supremacy, but not yet for verifiable & reliable computation

- Variational Quantum Algorithms – Use parmetrized quantum circuits that run on quantum computers and outsource the parameter optimization to a classical optimizer. [Cerezo *et al*., Nature Rev. Phys. 3, 625 (2021)]

- Quantum communication – technology to distribute quantum entalgment (secret key) is needed.

- Quantum sensing – relatively near-term high-impact applications

John Preskill, "Quantum computing in the NISQ era and beyond," Quantum 2, 79 (2019)[arXiv:1801.00862v3]

Quantum sensing (QS) and requirements

- Quantum sensors must have discrete and well-defined quantum states. Examples - polarization of photons, quantized currents in superconducting circuits, electronic or nuclear spin states

- It should be possible to initialize the sensor into a single and well-known states such that the desired stimulus produces a specific, predictable, and measurable outcomes

- Sensors must be addressable for manipulation, for example, by optical, microwave, or radio frequency waves

- Sensors must incorporate a sensor read-out pathway to measure the signal response

C.-J. Yu, …, D. E. Freedman, *ACS Cent. Sci.* **7**, 712 (2021)

- Quantum sensors must interact with the environment strongly enough so as to produce necessary changes. (major difference from quantum computation)

- Quantum sensors should be capable of generating coherent quantum states with long enough lifetimes because they enable the use of entanglement to boost sensor performance in multi-sensor or ensemble measurement.

C.-J. Yu, …, D. E. Freedman, *ACS Cent. Sci.* **7**, 712 (2021)

- Understanding and controlling open system quantum dynamics that leads to measurement or estimation process is a major issue

- Can there be other effective quantum sensing technique that does not rely heavily on entanglement, which is fragile and expensive to create?

- General theory for quantum sensing is needed.

Quantum (parameter) estimation

- Estimation of physical parameters or properties of a quantum system that cannot be measured directly either in principle or due to experimental difficulty.

- Examples are entanglement and purity for which there does not exist well-defined operator with physical observable.

- **Global Quantum Estimation** – Determine a single positive operator value measure (POVM) minimizing a suitable cost functional, which is averaged over all possible values of the parameters to be estimated, for example, estimation of global temperature scale [J. Rubio, Quantum Sci. Technol. **8**, 015009 (2022)]

- **Local Quantum Estimation** – Looks for the POVM maximizing the Fisher information, *i.e.*, minimizing the variance of the estimator at a fixed value of the parameter.

M. G. A. Paris, *Int. J. Quantum Information* **7**, 125-137 (2009)

Positive Operator Value Measure (POVM) Measurement

$$\int dx \, \boxed{\hat{\Pi}_{\boxed{x}}} = \hat{1}$$

Result of measurement

Hermitian and Positive operator

- POVM is more general than von Neumann's projection operator.
- POVM accounts for the cases where detailed post-measurement states do not have to be specified.
- Each component of a POVM for different values of *x* does not have to commute with the other component.

$$\langle\psi|\hat{\Pi}_x|\psi\rangle \geq 0 \text{ \& For } x \neq x', \ [\hat{\Pi}_x, \hat{\Pi}_{x'}] \neq 0 \text{ is possible}$$

POVM for Work Measurement

Work requires measurement at two times

$$\hat{H}(t_i)|\phi_{m,i}\rangle = E_{m,i}|\phi_{m,i}\rangle \ \& \ \hat{H}(t_f)|\phi_{m,f}\rangle = E_{m,f}|\phi_{m,f}\rangle$$

$$\hat{W}(w) = \sum_{n,m} |\langle\phi_{m,f}|\hat{U}(t_f, t_i)|\phi_{n,i}\rangle|^2 \delta\left(w - (E_{m,f} - E_{n,i})\right) |\phi_{n,i}\rangle\langle\phi_{n,i}|$$

$$\int dw \hat{W}(w) = \hat{1}$$

$$P(w) = \mathrm{Tr}\left\{\hat{W}(w)\hat{\rho}(t_i)\right\}$$

Same as the probability of work determined from two-time energy measurement

$$= \sum_{n,m} p_{n,i}|\langle\phi_{m,f}|\hat{U}(t_f, t_i)|\phi_{n,i}\rangle|^2 \delta\left(w - (E_{m,f} - E_{n,i})\right) |\phi_{n,i}\rangle\langle\phi_{n,i}|$$

Roncaglia, Cerisola, and Paz, *Phys. Rev. Lett.* **113**, 250601 (2014)

Theoretical issues with quantum sensing and quantum estimation

- Identification of appropriate POVM for desired estimation
- Identification of appropriate quantum states and transitions that maximize the precision of the estimation, which amounts to identifying states that maximizes the quantum Fisher information
- Relationship with thermodynamic uncertainty principle and quantum speed limit
- Accurate enough method for quantum dynamics simulation is essential for reliable prediction and verification of the outcome of sensing or estimation

(Classical) Cramer-Rao inequality

[Adapted from “Course note by A. Merberg and S. Miller https://web.williams.edu/Mathematics/sjmiller/public_html/BrownClasses/162/Handouts/CramerRaoHandout08.pdf”]

$p(x|\lambda)$: Probability density for a random variable x given a fixed parameter λ

For n_r random variables

$\xi_1, \xi_2, \cdots, \xi_{n_r}$ drawn from $p(x|\lambda)$,

assume that there exists an unbiased estimator

$E(\xi_1, \cdots, \xi_{n_r})$ such that

$$\lambda = \int dx_1 \int \cdots \int dx_{n_r}\ E(x_1, \cdots, x_{n_r}) \prod_{k=1}^{n_r} p(x_k|\lambda)$$

$$= \int d\mathbf{x}\ E(\mathbf{x}) P(\mathbf{x}|\lambda)$$

Assume that

$$\frac{\partial}{\partial\lambda}E(\mathbf{x}) = 0,$$

$$\sigma_\lambda \equiv \int d\mathbf{x}(E(\mathbf{x}) - \lambda)^2 P(\mathbf{x}|\lambda) < \infty$$

Since $P(\mathbf{x}|\lambda) = \prod_{k=1}^{n_r} p(x_k|\lambda)$ is normalized,

$$\int d\mathbf{x}\,(E(\mathbf{x}) - \lambda)\,P(\mathbf{x}|\lambda) = 0$$

Taking derivative with respect to λ

$$\int d\mathbf{x}\,(E(\mathbf{x}) - \lambda)\,\frac{\partial}{\partial\lambda}P(\mathbf{x};\lambda) - \overset{=1}{\boxed{\int d\mathbf{x} P(\mathbf{x};\lambda)}} = 0$$

Therefore,

$$\int d\mathbf{x}\,(E(\mathbf{x})-\lambda)\,P(\mathbf{x}|\lambda)\sum_{j=1}^{n_r}\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)=1$$

$$\begin{aligned}\frac{\partial}{\partial\lambda}P(\mathbf{x}|\lambda)&=\sum_{j=1}^{n_r}\left(\frac{\partial}{\partial\lambda}p(x_j|\lambda)\right)\prod_{k\neq j}^{n_r}p(x_k|\lambda)\\&=\sum_{j=1}^{n_r}\left(\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)\right)\prod_{k=1}^{n_r}p(x_k|\lambda)\\&=\sum_{j=1}^{n_r}\left(\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)\right)P(\mathbf{x}|\lambda)\end{aligned}$$

Taking square

$$\left[\int d\mathbf{x}\,(E(\mathbf{x})-\lambda)\,\sqrt{P(\mathbf{x}|\lambda)}\sqrt{P(\mathbf{x}|\lambda)}\left(\sum_{j=1}^{n_r}\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)\right)\right]^2=1$$

Applying Cauchy-Schwarz inequality,

$$\boxed{\left(\int d\mathbf{x}\,(E(\mathbf{x})-\lambda)^2\,P(\mathbf{x}|\lambda)\right)}\;\boxed{\left(\int d\mathbf{x}\;P(\mathbf{x}|\lambda)\Big(\sum_{j=1}^{n_r}\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)\Big)^2\right)}\geq 1$$

$$\uparrow$$

$$\sigma_\lambda$$

$$=\sum_{j=1}^{n_r}\int dx_1\cdots\int dx_{n_r}P(\mathbf{x}|\lambda)\left(\frac{\partial}{\partial\lambda}\ln p(x_j|\lambda)\right)^2$$

$$+\sum_{j=1}^{n_r}\sum_{k\neq j}\left(\frac{\partial}{\partial\lambda}\int\;dx_j p(x_j|\lambda)\right)\left(\frac{\partial}{\partial\lambda}\int dx_k\;p(x_k|\lambda)\right)$$

$$=n_r\int dx\;p(x|\lambda)\left(\frac{\partial}{\partial\lambda}\ln p(x|\lambda)\right)^2\equiv n_r F(\lambda)$$

Cramer-Rao inequality

$$\sigma_\lambda \geq \frac{1}{n_r F(\lambda)}$$

Number of random variables used to estimate λ

$$F(\lambda) = \int dx \; p(x|\lambda) \left(\frac{\partial}{\partial \lambda} \ln p(x|\lambda) \right)^2$$

$$= \int dx \frac{\left(\frac{\partial}{\partial \lambda} p(x|\lambda) \right)^2}{p(x|\lambda)}$$

Consider a quantum system with density operator $\hat{\rho}(\lambda)$, where λ represents a parameter that can be estimated.

Note that $$p(x|\lambda) = Tr\left\{\hat{\Pi}_x \hat{\rho}(\lambda)\right\}$$

$\hat{\Pi}_x$ is independent of λ $$\frac{\partial}{\partial\lambda} p(x|\lambda) = Tr\left\{\hat{\Pi}_x \frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right\}$$

Therefore, $$F(\lambda) = \int dx \frac{\left(\mathrm{Tr}\left\{\hat{\Pi}_x \frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right\}\right)^2}{\mathrm{Tr}\left\{\hat{\Pi}_x \hat{\rho}(\lambda)\right\}}$$

λ can be estimated from n_r random variables, $\xi_1, \xi_2, \cdots, \xi_{n_r}$, generated according to $p(x|\lambda)$, in terms of the same estimator, $E(\xi_1, \cdots, \xi_{n_r})$

$$\sigma_\lambda \geq \frac{1}{n_r F(\lambda)}$$

How to express $\mathrm{Tr}\left\{\hat{\Pi}_x \frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right\}$ in a form that involves $\mathrm{Tr}\left\{\hat{\rho}(\lambda)\cdots\right\}$

Define a symmetrization (with density operator) super-operator

$$\mathcal{R}_\rho(\hat{O}) \equiv \frac{1}{2}\left(\hat{O}\hat{\rho} + \hat{\rho}\hat{O}\right) = \sum_{j,k}\frac{1}{2}(p_j + p_k)O_{jk}|j\rangle\langle k|$$

Eigenstate of $\hat{\rho}$

Define an inverse symmetrization super-operator

$$[\mathcal{R}_\rho^{-1}(\hat{O})]_{jk} = \frac{2O_{jk}}{(p_j + p_k)}$$

Defined in the Hilbert space where $\hat{\rho} = \sum_j p_j|j\rangle\langle j|$ is nonzero.

Braunstein and Caves, *Phys. Rev. Lett.* 72, 3439 (1994)

Proof that $\mathcal{R}_\rho^{-1}$ is inverse of $\mathcal{R}_\rho$
for $\hat{O}$ that is complete in the domain where $\mathcal{R}_\rho^{-1}$ can be defined.

$$\begin{aligned}
\mathcal{R}_\rho^{-1}\left(\mathcal{R}_\rho(\hat{O})\right) &= \sum_{j,k} \frac{2}{(p_j + p_k)} \left(\mathcal{R}_\rho(\hat{O})\right)_{jk} |j\rangle\langle k| \\
&= \sum_{j,k} \frac{2}{(p_j + p_k)} \frac{(p_j + p_k)}{2} O_{jk} |j\rangle\langle k| \\
&= \hat{O} \\
\mathcal{R}_\rho\left(\mathcal{R}_\rho^{-1}(\hat{O})\right) &= \sum_{j,k} \frac{p_j + p_k}{2} \left(\mathcal{R}_\rho^{-1}(\hat{O})\right)_{jk} |j\rangle\langle k| \\
&= \sum_{j,k} \frac{(p_j + p_k)}{2} \frac{2}{(p_j + p_k)} O_{jk} |j\rangle\langle k| \\
&= \hat{O}
\end{aligned}$$

For any $\hat{A}$ and $\hat{B}$, which are complete
in the domain where $\mathcal{R}_\rho^{-1}$ can be defined

$$\mathrm{Tr}\left\{\hat{A}\hat{B}\right\} = \mathrm{Re}\left[\mathrm{Tr}\left\{\hat{\rho}\hat{A}\mathcal{R}_\rho^{-1}(\hat{B})\right\}\right]$$

Proof:

$$\hat{A}\mathcal{R}_\rho^{-1}(\hat{B}) = \sum_{j,k} \hat{A}\frac{2B_{jk}}{p_j + p_k}|j\rangle\langle k|$$

$$\Rightarrow \mathrm{Tr}\left\{\hat{\rho}\hat{A}\mathcal{R}_\rho^{-1}(\hat{B})\right\} = \sum_{j,k} p_k\frac{2B_{jk}}{(p_j + p_k)}A_{kj}$$

$$\left(\mathrm{Tr}\left\{\hat{\rho}\hat{A}\mathcal{R}_\rho^{-1}(\hat{B})\right\}\right)^* = \sum_{j,k} p_k\frac{2B^*_{jk}}{(p_j + p_k)}A^*_{kj}$$

$$= \sum_{j,k} p_k\frac{2B_{kj}}{(p_j + p_k)}A_{jk} = \sum_{j,k} p_j\frac{2B_{jk}}{(p_j + p_k)}A_{kj}$$

$$\mathrm{Re}\left[\mathrm{Tr}\left\{\hat{\rho}\hat{A}\mathcal{R}_\rho^{-1}(\hat{B})\right\}\right] = \sum_{j,k}\frac{1}{2}(p_j + p_k)\frac{2}{(p_j + p_k)}B_{jk}A_{kj} = \mathrm{Tr}\left\{\hat{A}\hat{B}\right\}$$

$$F(\lambda) = \int dx \frac{\left(\mathrm{Tr}\left\{\hat{\Pi}_x \frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right\}\right)^2}{\mathrm{Tr}\left\{\hat{\Pi}_x \hat{\rho}(\lambda)\right\}}$$

$$= \int dx \frac{\left(\mathrm{Re}\left[\mathrm{Tr}\left\{\hat{\rho}(\lambda)\hat{\Pi}_x \mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right\}\right]\right)^2}{\mathrm{Tr}\left\{\hat{\Pi}_x \hat{\rho}(\lambda)\right\}}$$

Since the square of a real number is smaller than the square of the absolute value of a complex number,

$$F(\lambda) \leq \int dx \frac{\left|\mathrm{Tr}\left\{\hat{\rho}(\lambda)\hat{\Pi}_x \mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right\}\right|^2}{\mathrm{Tr}\left\{\hat{\Pi}_x \hat{\rho}(\lambda)\right\}}$$

Define

$$\hat{A} = \frac{\hat{\rho}(\lambda)^{1/2}\hat{\Pi}_x^{1/2}}{\left(\mathrm{Tr}\left\{\hat{\Pi}_x\hat{\rho}(\lambda)\right\}\right)^{1/2}}$$

$$\hat{B} = \hat{\Pi}_x^{1/2}\mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\hat{\rho}(\lambda)^{1/2}$$

$$\int dx \frac{\left|\mathrm{Tr}\left\{\hat{\rho}(\lambda)\hat{\Pi}_x\hat{\mathcal{R}}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right\}\right|^2}{\mathrm{Tr}\left\{\hat{\Pi}_x\hat{\rho}(\lambda)\right\}}$$

$$= \int dx \frac{\left|\mathrm{Tr}\left\{\hat{\rho}(\lambda)^{1/2}\hat{\rho}(\lambda)^{1/2}\hat{\Pi}_x^{1/2}\hat{\Pi}_x^{1/2}\mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right\}\right|^2}{\mathrm{Tr}\left\{\hat{\Pi}_x\hat{\rho}(\lambda)\right\}}$$

$$= \int dx \left|\mathrm{Tr}\left\{\hat{A}\hat{B}\right\}\right|^2$$

$$\leq \int dx \overset{=1}{\boxed{\left|Tr\left\{\hat{A}\hat{A}^\dagger\right\}\right|}}\left|Tr\left\{\hat{B}\hat{B}^\dagger\right\}\right| = \int dx \left|Tr\left\{\hat{B}\hat{B}^\dagger\right\}\right|$$

Cauchy-Schwarz inequality

$$F(\lambda) \leq \int dx \ \mathrm{Tr} \left\{ \hat{\Pi}_x \mathcal{R}_\rho^{-1} \left(\frac{\partial}{\partial \lambda} \hat{\rho}(\lambda) \right) \hat{\rho}(\lambda) \mathcal{R}_\rho^{-1} \left(\frac{\partial}{\partial \lambda} \hat{\rho}(\lambda) \right) \right\}$$

$$= \mathrm{Tr} \left\{ \mathcal{R}_\rho^{-1} \left(\frac{\partial}{\partial \lambda} \hat{\rho}(\lambda) \right) \hat{\rho}(\lambda) \mathcal{R}_\rho^{-1} \left(\frac{\partial}{\partial \lambda} \hat{\rho}(\lambda) \right) \right\}$$

Note that $\int dx \ \hat{\Pi}_x = \hat{1}$

Combining this with the (classical) Cramer-Rao inequality,

$$\sigma_\lambda \geq \frac{1}{n_r F(\lambda)} \geq \frac{1}{n_r F_Q(\lambda)}$$

$$F_Q(\lambda) = Tr \left\{ \hat{\rho}(\lambda) \left(\mathcal{R}_\rho^{-1} \left(\frac{\partial}{\partial \lambda} \hat{\rho}(\lambda) \right) \right)^2 \right\}$$

$$F_Q(\lambda) = Tr\left\{\hat{\rho}(\lambda)\left(\mathcal{R}_{\rho}^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right)^2\right\}$$

$$= \sum_j \sum_k p_j \frac{2\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)_{jk}}{(p_j + p_k)} \frac{2\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)_{kj}}{(p_j + p_k)}$$

$$= \sum_j \sum_k \frac{p_j + p_k}{2} \frac{2\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)_{jk}}{(p_j + p_k)} \frac{2\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)_{kj}}{(p_j + p_k)}$$

$$= \sum_j \sum_k \frac{2}{(p_j + p_k)} \left|\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)_{jk}\right|^2$$

Estimation is bounded by intrinsic property of the density operator and parameter, not the type of measurement used for estimation!

Braunstein and Caves, Phys. Rev. Lett. 72, 3439 (1994)

$$F(\lambda) = F_Q(\lambda) \text{ if}$$

$$\mathrm{Im}\left[\mathrm{Tr}\left\{\hat{\rho}(\lambda)\hat{\Pi}_x\mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right\}\right] = 0, \&$$

$$\hat{\Pi}_x^{1/2}\hat{\rho}(\lambda)^{1/2} = C_x\hat{\Pi}_x^{1/2}\mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\hat{\rho}(\lambda)^{1/2}$$

➡ $\hat{\Pi}_x^{1/2}\left(\hat{1} - C_x\mathcal{R}_\rho^{-1}\left(\frac{\partial}{\partial\lambda}\hat{\rho}(\lambda)\right)\right) = 0 \text{ \& } C_x \text{ is a real number}$

➡ Distinguishability metric for density operator &
General uncertainty relation for estimating parameter λ

Jones and Kok, “Geometric derivation of the quantum spped limit,” Phys. Rev. A **82**, 022107 (2010)

Derivation of Mandelstam-Tamm inequality

Time required for a quantum system to naturally evolve to an orthogonal state

$$t \geq \frac{\pi}{2} \frac{\hbar}{\sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}},$$

Derivation of Margolus-Levitin inequality

$$t \geq \frac{\pi}{2} \frac{\hbar}{\langle \hat{H} - E_g \rangle},$$

Applications of Quantum Fisher Information to quantum metrology, quantum sensing, and quantum thermodynamics

- M. G. Paris, ″Quantum estimation for quantum technology,″ *Int. J. Quantum Information* **7**, 125-137 (2009)
- Jing Liu *et al*., "Quantum Fisher information matrix and multiparameter estimation,″ *J. Phys. A: Math. Theor*. **53,** 023001 (2020)
- Hasegawa, "Thermodynamic uncertainty relation for general open quantum systems," *Phys. Rev. Lett.* **126**, 010602 (2021) – with additional Lindblad dynamics and continuous time measurement

Issues with the Proof of Quantum Thermodynamic Uncertainty Relation for Open system Quantum Dynamics

- Definition of total entropy production is not well understood, especially considering the effect of correlation (entanglement) between system and reservoir

- Exact details of the underlying quantum dynamics for open system, which can be detrimental for entropy production and the actual time dependences of physical observables, are not well-known.

- Most theoretical results are based on Lindblad equation and the resulting continuous time measurement formulation. While these are axiomatically correct, to what extent they represent the dynamics of real system is not clear.

Entropy Production in Open System Quantum Dynamics

[Esposito et al. New J. Phys. 12, 013013 (2010)]

$$\hat{H}(t) = \hat{H}_s(t) + \sum_r \hat{H}_r + \hat{V}(t)$$

$$\hat{\rho}(0) = \hat{\rho}_s(0) \prod_r \hat{\rho}_r^{eq}$$

$$\hat{\rho}_r(0) = \hat{\rho}_r^{eq} = \frac{\exp(-\beta_r \hat{H}_r)}{Z_r}$$

$$S(0) = -Tr_s \left\{\hat{\rho}_s(0) \ln \hat{\rho}_s(0)\right\} - \sum_r Tr_r \left\{\hat{\rho}_r^{eq} \ln \hat{\rho}_r^{eq}\right\}$$

$$S(t) = -Tr\left\{\hat{\rho}(t)\ln\hat{\rho}(t)\right\}$$
$$= -Tr\left\{\hat{U}(t)\hat{\rho}(0)\ln\hat{\rho}(0)\hat{U}^{\dagger}(t)\right\} = S(0)$$

$$\hat{U}(t) = \exp_{(+)}\left\{-\frac{i}{\hbar}\int_0^t d\tau\hat{H}(\tau)\right\}$$

Note that $S(0) = -Tr_s\left\{\hat{\rho}_s(0)\ln\hat{\rho}_s(0)\right\} - \sum_r Tr_r\left\{\hat{\rho}_r^{eq}\ln\hat{\rho}_r^{eq}\right\}$

$$-Tr_s\left\{\hat{\rho}_s(0)\ln\hat{\rho}_s(0)\right\} = -\,Tr\left\{\hat{\rho}(t)\ln\hat{\rho}(t)\right\}$$
$$+\sum_r Tr_r\left\{\hat{\rho}_r^{eq}\ln\hat{\rho}_r^{eq}\right\}$$

Let us define $\Delta S_s(t) \equiv S_s(t) - S_s(0)$

$$= -Tr_s\left\{\hat{\rho}_s(t)\ln\hat{\rho}_s(t)\right\} + Tr_s\left\{\hat{\rho}_s(0)\ln\hat{\rho}_s(0)\right\}$$

$$
\begin{aligned}
\Delta S_s(t) = & - Tr_s \left\{ \hat{\rho}_s(t) \ln \hat{\rho}_s(t) \right\} + Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}(t) \right\} \\
& - \sum_r Tr_r \left\{ \hat{\rho}_r^{eq} \ln \hat{\rho}_r^{eq} \right\} \\
= & - Tr_s \left\{ Tr_{\{r\}} \left\{ \hat{\rho}(t) \right\} \ln \hat{\rho}_s(t) \right\} + Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}(t) \right\} \\
& - \sum_r Tr_r \left\{ \hat{\rho}_r^{eq} \ln \hat{\rho}_r^{eq} \right\} \\
= & - Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}_s(t) \right\} + Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}(t) \right\} \\
& - \sum_r Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}_r^{eq} \right\} \\
& - \sum_r Tr_r \left\{ \hat{\rho}_r^{eq} \ln \hat{\rho}_r^{eq} \right\} + \sum_r Tr \left\{ \hat{\rho}(t) \ln \hat{\rho}_r^{eq} \right\}
\end{aligned}
$$

$$\Delta S_s(t) = -\,Tr\left\{\hat{\rho}(t)\ln\left(\hat{\rho}_s(t)\prod_r \hat{\rho}_r^{eq}\right)\right\} + Tr\left\{\hat{\rho}(t)\ln\hat{\rho}(t)\right\}$$
$$-\sum_r Tr_r\left\{\hat{\rho}_r^{eq}\ln\hat{\rho}_r^{eq}\right\} + \sum_r Tr_r\left\{\hat{\rho}_r(t)\ln\hat{\rho}_r^{eq}\right\}$$

Note that $\hat{\rho}_r(t) \equiv Tr_{s,\{r'\neq r\}}\left\{\hat{\rho}(t)\right\}$

$$\Delta S_s(t) = \Delta_i S_s(t) + \Delta_e S_s(t)$$

$$\Delta_i S_s(t) = Tr\left\{\hat{\rho}(t)\ln\left(\frac{\hat{\rho}(t)}{\hat{\rho}_s(t)\prod_r \hat{\rho}_r^{eq}}\right)\right\}$$
$$\equiv D\left[\hat{\rho}(t)||\hat{\rho}_s(t)\prod_r \hat{\rho}_r^{eq}\right]$$

Relative quantum
entropy production

$$\Delta_e S_s(t) = \sum_r Tr_r \left\{ \left(\hat{\rho}_r(t) - \hat{\rho}_r^{eq} \right) \ln \hat{\rho}_r^{eq} \right\}$$

External contribution to quantum entropy production of system

$$= -\sum_r \beta_r Tr_r \left\{ \left(\hat{\rho}_r(t) - \hat{\rho}_r^{eq} \right) \hat{H}_r \right\}$$

$$\equiv \sum_r \beta_r Q_r(t)$$

Heat flow from reservoir

In general, $\Delta_i S_s(t) = D\left[\hat{\rho}(t) || \hat{\rho}_s(t) \prod_r \hat{\rho}_r^{eq} \right] \geq 0$

This is a special case of

$$D[\hat{\rho}||\hat{\rho}'] = Tr\left\{ \hat{\rho} \ln \hat{\rho} - \hat{\rho} \ln \hat{\rho}' \right\} \geq 0$$

Quantum Kullback-Leibler divergence

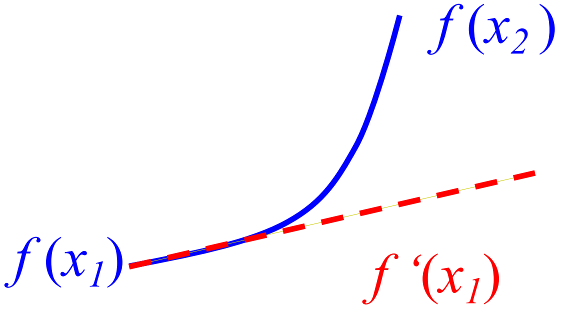
More generally, we can show the following inequality

$$D_f(\hat{A},\hat{B}) = Tr\left\{ f(\hat{A}) - f(\hat{B}) - (\hat{A}-\hat{B})f'(\hat{B}) \right\} \geq 0$$

where $f(x)$ is any convex function of x.

$$f(x_2) \geq f(x_1) + (x_2 - x_1)f'(x_1)$$

for any x_1 and x_2



Let us denote the complete sets of eigenstates of $\hat{A}$ and $\hat{B}$ respectively as $|\phi_i\rangle$'s and $|\psi_i\rangle$'s

$$\hat{A}|\phi_i\rangle = a_i|\phi_i\rangle \ \& \ \hat{B}|\psi_i\rangle = b_i|\psi_i\rangle$$

$$D_f(\hat{A},\hat{B})=\sum_i\langle\phi_i|f(\hat{A})-f(\hat{B})-(\hat{A}-\hat{B})f'(\hat{B})|\phi_i\rangle$$

$$=\sum_i\Big\{f(a_i)-\langle\phi_i|f(\hat{B})|\phi_i\rangle$$

$$-a_i\langle\phi_i|f'(\hat{B})|\phi_i\rangle+\langle\phi_i|\hat{B}f'(\hat{B})|\phi_i\rangle\Big\}$$

Expanding all the operators involving $\hat{B}$ with respect to $|\psi_j\rangle$'s

$$=\sum_i\sum_j\boxed{\{f(a_i)-f(b_j)-(a_i-b_j)f'(b_j)\}}\boxed{|\langle\phi_i|\psi_j\rangle|^2}$$

Nonnegative because *f(x)* is a convex function.

Nonnegative

Therefore, $D_f(\hat{A},\hat{B})\geq 0$

Consider $\boxed{f(x) = x \ln x}$, $\hat{A} = \hat{\rho}$, & $\hat{B} = \hat{\rho}'$

Convex function for $x > 0$

$$\begin{aligned} D_f(\hat{\rho}, \hat{\rho}') &= Tr\{\hat{\rho} \ln \hat{\rho} - \hat{\rho}' \ln \hat{\rho}' - (\hat{\rho} - \hat{\rho}')(\ln \hat{\rho}' + 1)\} \\ &= Tr\{\hat{\rho} \ln \hat{\rho} - \hat{\rho}' \ln \hat{\rho}' - \hat{\rho} \ln \hat{\rho}' + \hat{\rho}' \ln \hat{\rho}'\} \\ &= Tr\{\hat{\rho} \ln \hat{\rho} - \hat{\rho} \ln \hat{\rho}'\} = D[\hat{\rho}||\hat{\rho}'] \geq 0 \end{aligned}$$

Equality holds when $\hat{\rho} = \hat{\rho}'$

This means that $\Delta S_i(t) = 0$ if

$$\hat{\rho}(t) = \hat{\rho}_s(t) \prod_r \hat{\rho}_{r,eq} = Tr_{\{r\}}\{\hat{\rho}(t)\} \prod_r \hat{\rho}_{r,eq}$$

Thus, $\Delta S_i(t)$ represents entropy production
due to mutual correlation between system and reservoir.

Further generalization

$$\Delta S_s(t) = -\,Tr\left\{\hat{\rho}(t)\ln\left(\hat{\rho}_s(t)\prod_r \hat{\rho}_r^{eq}\right)\right\} + Tr\left\{\hat{\rho}(t)\ln\hat{\rho}(t)\right\}$$

$$-\sum_r Tr_r\left\{\hat{\rho}_r^{eq}\ln\hat{\rho}_r^{eq}\right\} + \sum_r Tr_r\left\{\hat{\rho}_r(t)\ln\hat{\rho}_r^{eq}\right\}$$

This identity holds even when $\hat{\rho}_r^{eq}$ is replaced with $\hat{\rho}_r(0)$

Therefore, $\Delta S_s(t) = \Delta_i S_s(t) + \Delta_e S_s(t)$

$$\Delta_i S_s(t) = Tr\left\{\hat{\rho}(t)\ln\left(\frac{\hat{\rho}(t)}{\hat{\rho}_s(t)\prod_r \hat{\rho}_r(0)}\right)\right\}$$

$$\equiv D\left[\hat{\rho}(t)||\hat{\rho}_s(t)\prod_r \hat{\rho}_r(0)\right]$$

$$\Delta_e S_s(t) = \sum_r Tr_r\left\{(\hat{\rho}_r(t) - \hat{\rho}_r(0))\ln\hat{\rho}_r(0)\right\}$$

Recent Works on Entropy Production and Quantum Fluctuations in Open System Quantum Dynamics utilizing the general relationship: $\Delta S_s(t) = \Delta_i S_s(t) + \Delta_e S_s(t)$

- Manzano *et al.*, "Quantum fluctuation theorems for arbitrary environments: Adiabatic and nonadiabatic entropy production, Phys. Rev. X **8**, 031037 (2018)
- Landi and Paternostro, "Irreversible entropy production: From classical to quantum," Revs. Mod. Phys. **93**, 035008 (2021)

Challenges for Theoretical Understanding of Entropy Production for General Open System Quantum Dynamics

- Exact calculation of system entropy production still requires information on full dynamics of the system and reservoirs. This means reformulation of traditional open system quantum dynamics approach in order to extract the missing information.

- The majority of the dynamics being employed, Lindblad dynamics, although axiomatically correct and easy to work with, relies on the assumption of extremely weak system-bath coupling and/or coarse-graining in time. What are real effects of these on actual dynamics and entropy production are not well understood.

Lindblad Equation – A form of Markovian quantum Master equation (QME) for system density operator

[G. Lindblad, Commun. Math. Phys. 48, 119 (1976)]

$$
\begin{aligned}
\frac{d}{dt}\hat{\rho}_s &= -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s] + \frac{1}{2}\sum_{\alpha}[\hat{L}_\alpha\hat{\rho}_s,\hat{L}_\alpha^\dagger] + \frac{1}{2}\sum_{\alpha}[\hat{L}_\alpha,\hat{\rho}_s\hat{L}_\alpha^\dagger] \\
&= \underbrace{\boxed{-\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s]}}_{\text{System Dynamics}} + \underbrace{\boxed{\frac{1}{2}\sum_{\alpha}\left\{2\hat{L}_\alpha\hat{\rho}_s\hat{L}_\alpha^\dagger - \hat{L}_\alpha^\dagger\hat{L}_\alpha\hat{\rho}_s - \hat{\rho}_s\hat{L}_\alpha^\dagger\hat{L}_\alpha\right\}}}_{\text{Effects of reservoir/environment/bath}}
\end{aligned}
$$

- This form of QME is necessary and sufficient condition for the direct product of the density operator and identity operator for its reservoir, with arbitrary degrees of freedom, to remain always positive – **complete positivity**

- This assumes instantaneous relaxation and/or entanglement of the environment.

  What is the entropy production for such relaxation?

Quantum Master Equation (QME) – Markovian form

Lindblad Eqn., Redfield Eqn. (2^{nd} order & Markovian appro.), …

$$\frac{d}{dt}\hat{\rho}_s(t) = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_s(t)] + \mathcal{R}\hat{\rho}_s(t)$$

No Markovian QME satisfies all of the following three requirements.

1. To remain positive semi-definite (no negative eigenvalues).
2. To approach an appropriate equilibrium state at long times.
3. To satisfy the principle of translational invariance (position independent friction).

Redfield equation – non-positive & can be made positive by secular approximation (ignoring non-resonant off-diagonal components) but then violates 3.

Lindblad equation – does not satisfy 2 or 3.

Kohen *et al. J. Chem. Phys.* **107**, 5236 (1997)

Debates between Pechukas and Alicki on Complete Positivity of Markovian QME

- **Pechukas**, “Reduced dynamics need not be completely positive, *Phys. Rev. Lett*. **73**, 1060 (1994)
- **Alicki**, *Phys. Rev. Lett*. **75**, 3020 (1995): Comment
- **Pechukas**, *Phys. Rev. Lett*. **75**, 3021 (1995): Reply

Consider $\hat{\rho}_s \to \Lambda\hat{\rho}_s = Tr_r \left\{ \hat{U}\Phi(\hat{\rho}_s)\hat{U}^\dagger \right\}$

Desired properties of Φ, which maps a system state to a pure state in system plus reservoir

(a) Φ preserves mixture

(b) $\mathrm{Tr}_r \{\Phi\hat{\rho}_s\} = \hat{\rho}_s$

(c) $\Phi(\hat{\rho}_s)$ is positive for all positive $\hat{\rho}_s$

The only mapping that satisfies all is direct product map: $\Phi(\hat{\rho}_s) = \hat{\rho}_s \otimes \hat{\rho}_r$

Debates between Pechukas and Alicki on Complete Positivity of Markovian QME

- **Pechukas**, "Reduced dynamics need not be completely positive, *Phys. Rev. Lett*. **73**, 1060 (1994)
- **Alicki**, *Phys. Rev. Lett*. **75**, 3020 (1995): Comment
- **Pechukas**, *Phys. Rev. Lett*. **75**, 3021 (1995): Reply

Pechukas: "Product map is valid only for weak coupling and does not represent many important and real physical situations. Therefore, complete positivity has to be abandoned because other properties cannot be given up. This is possible by limiting the domain of system states."

Alicki: "Complete positivity is essential and finding the exact condition for the positivity preserving domain is not possible. Rather, condition (a) or (b) can be given up.

Pechukas: "There is more serious physical issue by giving up (a) or (b), and it is OK to give up complete positivity for practical purposes."

Other debates on complete positivity and more recent theoretical works addressing this issue

Vacchini [*Phys. Rev. Lett.* **84**, 1374 (2000)]: Derivation of completely positive equation based on Boltzman type operators → Debate between O'Connell [*PRL* **87**, 028901 (2001)] and Vacchini [*PRL* **87**, 028902-1 (2001)].

Vacchini's eqn. does not lead to the canonical distribution of unperturbed system Hamiltonian. Ford and O'Connell's work [*PRL* **82**, 3376 (1999)] does so but is based on rotating wave Hamiltonian that does not satisfy translational invariance.

- Lindblad, "Brownian motion of quantum harmonic oscillators," J. Math. Phys. 39, 2763 (1998)
- Farina and Giovannetti, "Open-quantum-system dynamics: Recovering positivity of the Redfield equation via partial secular approximation," Phys. Rev. A 100, 012107 (2019)
- Trushechkin, "Unified Gorini-Kossakowski-Lindblad-Sudarshan quantum master equation beyond the secular approximation," Phys. Rev. A 103, 062226 (2021)

Derivation of formally exact QME

$$\frac{d}{dt}\hat{\rho}(t) = -i\hat{\mathcal{L}}(t)\hat{\rho}(t) \equiv -\frac{i}{\hbar}[\hat{H}(t), \hat{\rho}(t)]$$

$$\hat{H}(t) = \hat{H}_0(t) + \hat{H}_1(t)$$

Consider in the interaction picture with respect to the zeroth order Hamiltonian

$$\hat{U}_0(t, t_0) = e_{(+)}^{-i\int_{t_0}^{t} d\tau \hat{H}_0(\tau)/\hbar} \equiv 1 - \frac{i}{\hbar}\int_{t_0}^{t} d\tau \hat{H}_0(\tau) + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \hat{H}_0(\tau)\hat{H}_0(\tau') + \cdots$$

$$\frac{d}{dt}\hat{\rho}_I(t) = -i\hat{\mathcal{L}}_{1,I}(t)\hat{\rho}_I(t) \equiv -\frac{i}{\hbar}[\hat{H}_{1,I}(t), \hat{\rho}_I(t)]$$

$$\hat{H}_{1,I}(t) = \hat{U}_0^{\dagger}(t, t_0)\hat{H}_1(t)\hat{U}_0(t, t_0), \& \ \hat{\rho}_I(t) = \hat{U}_0^{\dagger}(t, t_0)\hat{\rho}(t)\hat{U}_0(t, t_0)$$

Projection super-operator: $\mathcal{P}$

$\mathcal{P}\hat{\rho}_I(t)$ contains all the information needed.

Complement: $\mathcal{Q} = 1 - \mathcal{P}$

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)(\mathcal{P}+\mathcal{Q})\hat{\rho}_I(t) = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t)$$

$\boxed{\text{Assume } \mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{P} = 0}$

This can always be satisfied by appropriate definition of $\hat{H}_1(t)$

$$\frac{d}{dt}\mathcal{Q}\hat{\rho}_I(t) = -i\mathcal{Q}\hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t) - i\mathcal{Q}\hat{\mathcal{L}}_{1,I}(t)\mathcal{P}\hat{\rho}_I(t)$$

$$\frac{d}{dt}\mathcal{Q}\hat{\rho}_I(t) + i\mathcal{Q}\hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(t) = -i\mathcal{Q}\hat{\mathcal{L}}_{1,I}(t)\mathcal{P}\hat{\rho}_I(t)$$

$$\mathcal{Q}\hat{\rho}_I(t) = -i\int_{t_0}^{t} d\tau\ e_{(+)}^{-i\int_{\tau}^{t} d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}\hat{\rho}_I(\tau) \\ + e_{(+)}^{-i\int_{t_0}^{t} d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}_I(t_0)$$

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = -\int_{t_0}^{t} d\tau\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)e_{(+)}^{-i\int_{\tau}^{t} d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\hat{\mathcal{L}}_I(\tau)\mathcal{P}\hat{\rho}_I(\tau) \\ - i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)e_{(+)}^{-i\int_{t_0}^{t} d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(t_0)$$

Formally exact time-nonlocal (TN) equation for

$$\hat{\rho}_I(\tau) = e_{(-)}^{i\int_\tau^t d\tau' \mathcal{L}_{1,I}(\tau')} \hat{\rho}_I(t)$$

Going backward in time is always well defined for the total density operator because every dynamics is unitary.

$$\mathcal{Q}\hat{\rho}_I(t) = -i\int_{t_0}^{t} d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')} \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \hat{\mathcal{L}}_{1,I}(\tau')} \hat{\rho}_I(t)$$
$$+ e_{(+)}^{-i\int_{t_0}^t d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)} \mathcal{Q}\hat{\rho}(t_0)$$

Insert $\mathcal{P}+\mathcal{Q}=1$

F. Shibata and T. Arimitsu, *J. Phys. Soc. Jpn.* ***49***, 891 (1980)

$$\mathcal{Q}\hat{\rho}_I(t) = (1 + i\hat{\Gamma}_{1,I}(t,t_0))^{-1}\left\{-i\int_{t_0}^{t} d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')} \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \hat{\mathcal{L}}_{1,I}(\tau')} \mathcal{P}\hat{\rho}_I(t)\right.$$
$$\left. + e_{(+)}^{-i\int_{t_0}^t d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)} \mathcal{Q}\hat{\rho}(t_0)\right\}$$

$$\hat{\Gamma}_{1,I}(t,t_0) = \int_{t_0}^{t} d\tau e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')} \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau' \hat{\mathcal{L}}_{1,I}(\tau')}$$

$$\begin{aligned}\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = &-\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)(1+i\hat{\Gamma}_{1,I}(t,t_0))^{-1}\\ &\times \int_{t_0}^{t} d\tau e_{(+)}^{-i\int_{\tau}^{t} d\tau' \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_{\tau}^{t} d\tau' \hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{P}\hat{\rho}_I(t)\\ &-i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)(1+i\hat{\Gamma}_{1,I}(t,t_0))^{-1}e_{(+)}^{-i\int_{t_0}^{t} d\tau \mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(t_0)\end{aligned}$$

Formally exact time-local (TL) equation for

$$\mathcal{P}(\cdot) = \hat{\rho}_b Tr_b\left\{(\cdot)\right\} \rightarrow \text{ QME for system density operator}$$

$$\mathcal{P}(\cdot) = \sum_k |\varphi_k\rangle\langle\varphi_k|\hat{\rho}_b^k \; Tr\{|\varphi_k\rangle\langle\varphi_k|(\cdot)\} \rightarrow \text{ME for population}$$

- Time-local form can account for all the non-Markovian effect and does not necessarily means more approximate than time-nonlocal (convolution form).
- QME for system density operator can be derived by going back to Schrödinger picture in the system space.

Redfield equation – 2nd order Markovian QME

$$\begin{aligned}\frac{d}{dt}\mathcal{P}\hat{\rho}_I(t) = &-\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)(1+i\hat{\Gamma}_{1,I}(t,t_0))^{-1}\\ &\times\int_{t_0}^{t} d\tau e_{(+)}^{-i\int_{\tau}^{t} d\tau'\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_{\tau}^{t} d\tau'\hat{\mathcal{L}}_{1,I}(\tau')}\mathcal{P}\hat{\rho}_I(t)\\ &-i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)(1+i\hat{\Gamma}_{1,I}(t,t_0))^{-1}e_{(+)}^{-i\int_{t_0}^{t} d\tau\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)}\mathcal{Q}\hat{\rho}(t_0)\end{aligned}$$

$$\mathcal{P}(\cdot) = \hat{\rho}_b Tr_b\left\{(\cdot)\right\} \rightarrow \text{ QME for system density operator}$$

- 2nd order approximation with respect to the interaction term.
- Markvoian approximation, i.e., send the integral to infinite.
- Go back to the Schrödinger picture with respect to the system Hamiltonian.

Four major numerical approaches for nearly exact open system quantum dynamics

- **Hierarchy of density operators:** For certain class of baths that can be modeled single or multiple exponentially decaying functions in time, it is possible to expand all the higher order terms as a hierarchy of auxiliary density-like operators. (**Y. Tanimura, Y. Yan, Q. Shi,** …)

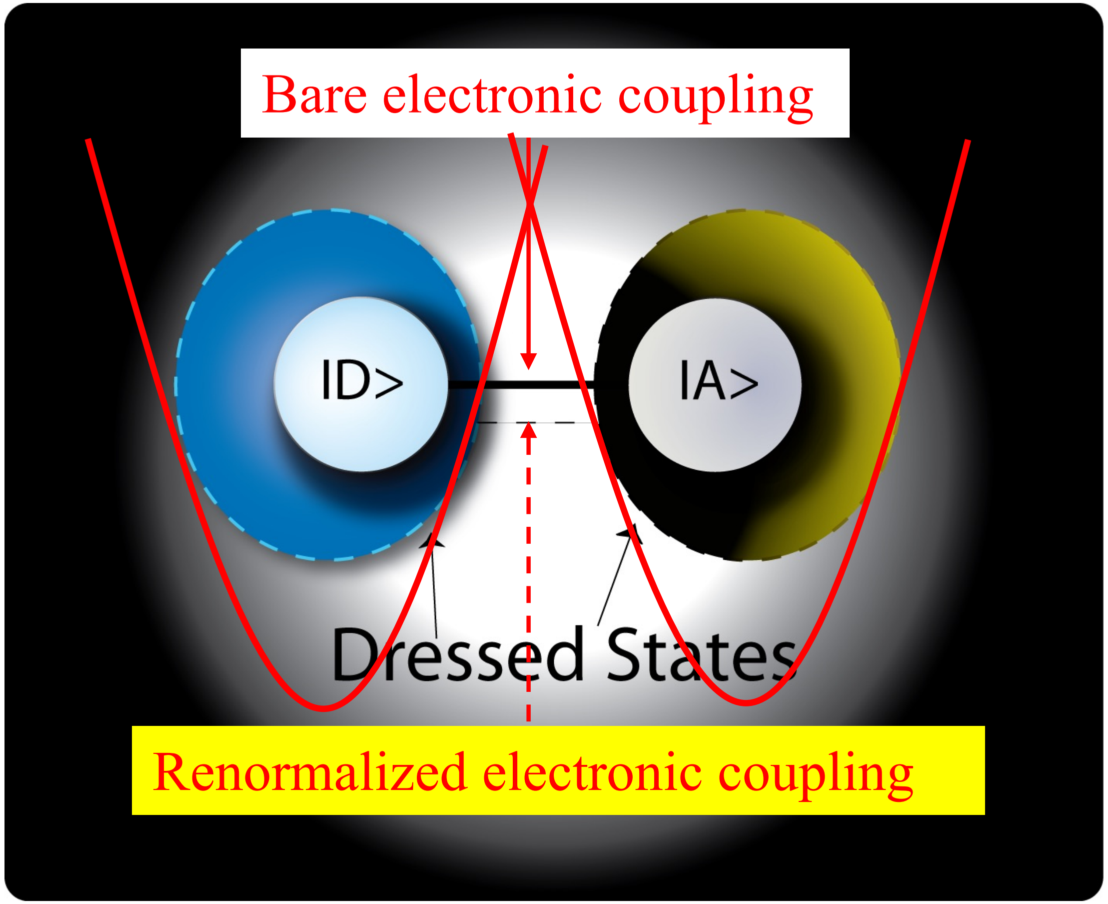
- **Generalized QME**: It is possible to derive an exact intego-differential equation for the unprojected part, which then can be simulated or approximated. (**Q. Shi, E. Geva, E. Rabani, D. Reichman, T. Markland,** …).

- Within the **path integral** formulation, the environmental effect can be accounted by **influence functional**, which can be calculated or simulated (**C. Mak, N. Makri,…**)

- It is possible to devise **tensor product equation** for general open system quantum dynamics, for which the tensor mapping can be learned from exact calculation or machine learning (**J.Cao, E. Geva, V. Batista**,…)

Polaron in charge & exciton (excitation energy) transfer/transport dynamics

Landau & Pekar, Fröhlich, Holstein, Feynman, … : dressed states for charge carriers



Renormalization of electronic coupling: Reduction due to *Franck-Condon overlap factors* of two displaced oscillators

Silbey and coworkers : dressed states for excitation energy transfer, unified treatment of incoherent and coherent dynamics

Polaron transformed quantum master equation approach

1. Make polaron-transformation (system dependent displacement of harmonic oscillator bath) – Unitary transformation in the total system plus bath space.
2. Redefine a small perturbation term.
3. Application of projection operator and make perturbation approximation to obtain a practical time dependent QME.

Important detail not to overlook

The initial condition and physical observable should also be transformed accordingly in order not to change the nature of physical conditions and observables being measured.

PQME for exciton dynamics (2^{nd} order time-local in the interaction picture)

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$

S. Jang, Y.-C. Cheng, D. Reichman, and J. D. Eaves, *J. Chem. Phys.*, **129**, 101104 (2008)

S. Jang, *J. Chem. Phys.* **131**, 164101 (2009) : Coherent initial condition

S. Jang, *J. Chem. Phys.* **135**, 034105 (2011) : Multistate system

L. Yang, M. Devi, S. Jang, *J. Chem. Phys.*, **137**, 024101 (2012): non-Condon effect

S. Jang, T. Berkelbach, and D. R. Reichman, *New. J. Phys.*, **15**, 105020 (2012): Application to donor-bridge-acceptor system

S. Jang, *J. Phys. Chem. C* **123**, 5767 (2019) : Distance dependence of FRET

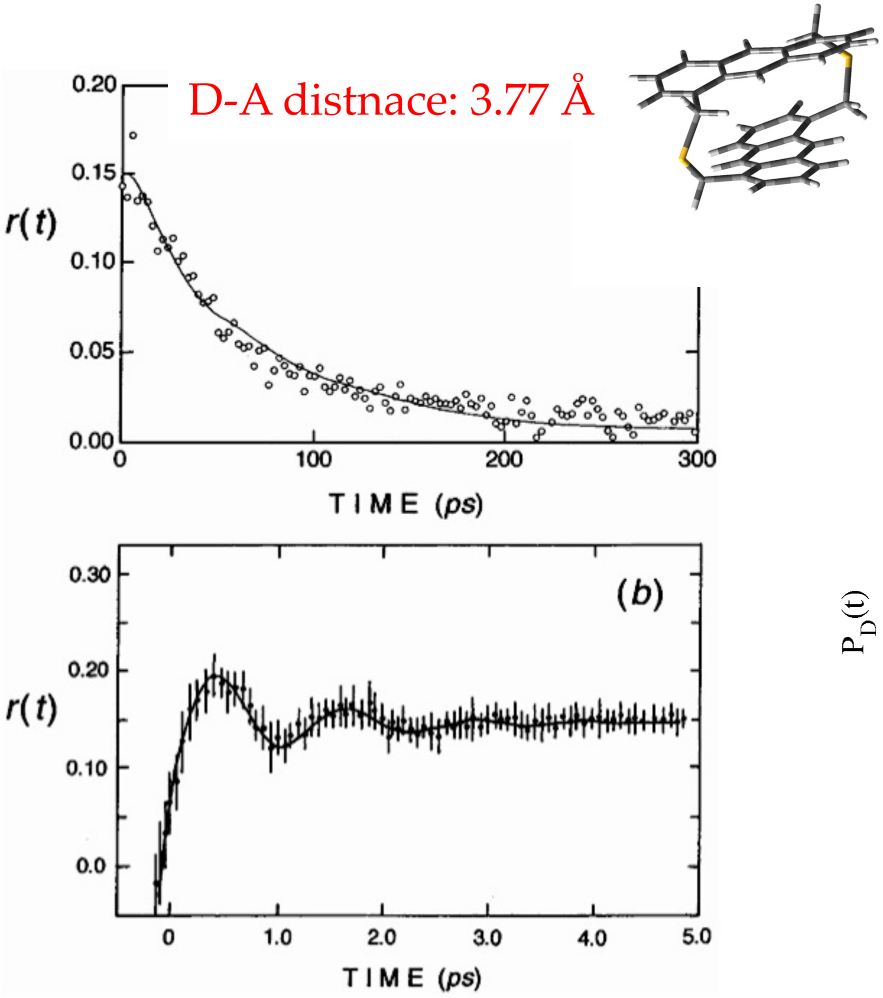
S. Jang, Chap. 9 in *Ultrafast Dynamics at the Nanoscale (Eds. Haacke and Burghardt, Pan Stanford)* (2016)

S. J. Jang, *Dynamics of Molecular Excitons (Elsevier)* (2020)

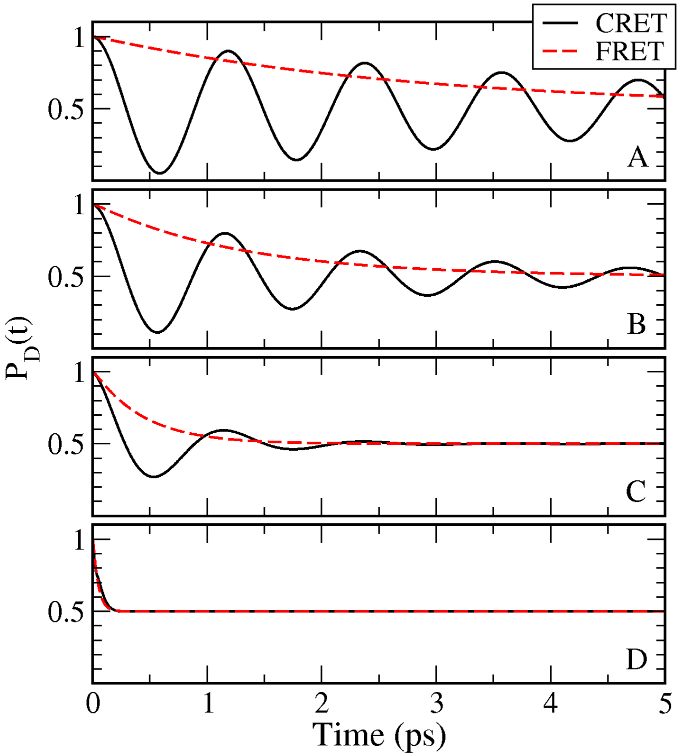
Works by Yuan-Chung Cheng, Ahsan Nazir, Jianshu Cao, Ivan Kassal, ….

Application to intramolecular exciton dynamics

Expeirmental dephasing time (1ps) and period of oscillation (1.2 ps)
can be reproduced by moderate polaronic effect and $J = 50 - 100\ \mathrm{cm}^{-1}$



	A	B	C	D
J (cm^{-1})	53.5	66.8	100	334
J' (cm^{-1})	24	30	45	150
$\omega_c/(2\pi c)$ (cm^{-1})	500	400	300	200
η	2.4	3	4	6



$$J' = 0.449J$$

Debye-Waller factor of high frequency vibrational modes

Yang, Caprasecca, Mennucci, and Jang, *J. Am. Chem. Soc.* **132**, 16911 (2010)

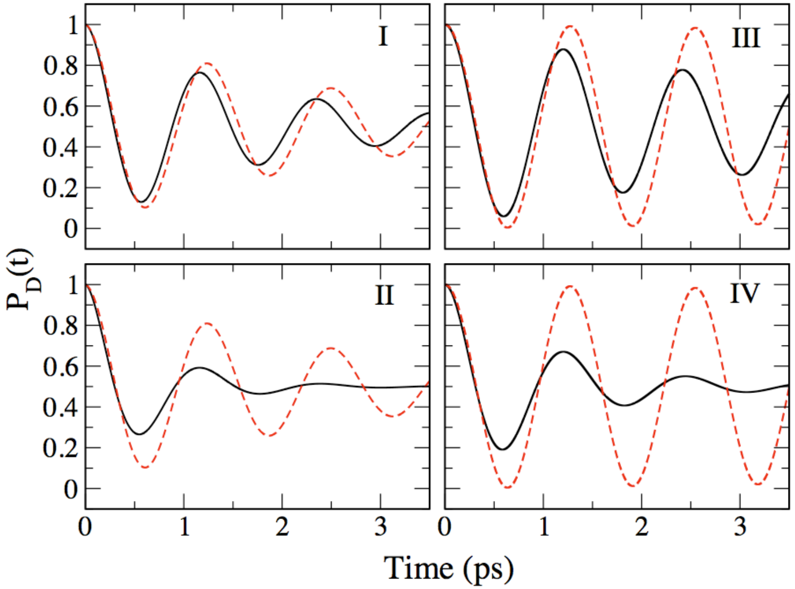
PQME with non-Condon (or inelastic) effects

$$H = E_D|D\rangle\langle D| + E_A|A\rangle\langle A| + J(|D\rangle\langle A| + |A\rangle\langle D|) + \sum_n \hbar\omega_n (g_{nD}|D\rangle\langle D| + g_{nA}|A\rangle\langle A|) + \sum_n \hbar\omega_n \left(b_n^\dagger b_n + \frac{1}{2}\right)$$

$$J = C_0 + C_1 \sin(\phi - \phi_0)$$

$$\phi = \sum_n g_{n\phi}(b_n + b_n^\dagger)$$

$$\mathcal{J}_\phi(\omega) = \sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n\phi}^2 = \frac{1}{6}\frac{\omega^3}{\omega_{c\phi}^2} e^{-\omega/\omega_{c,\phi}}$$



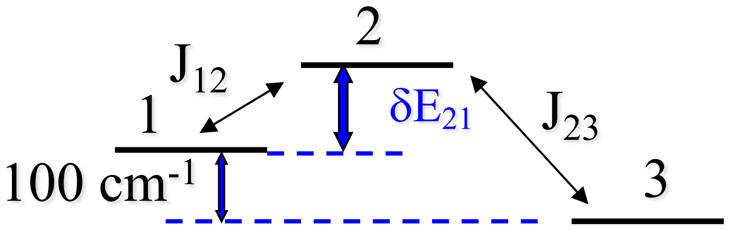
	C_0 (cm^{-1})	C_1 (cm^{-1})
I	30	-10
II	30	-30
III	20	-10
IV	20	-20

Torsional modulation of electronic coupling by bath increase dephasing and relaxation rates but details of its amplitude and reference (zero coupling) angle have important effects.

Yang, Devi, and Jang, *J. Chem. Phys.* **137**, 024101 (2012)

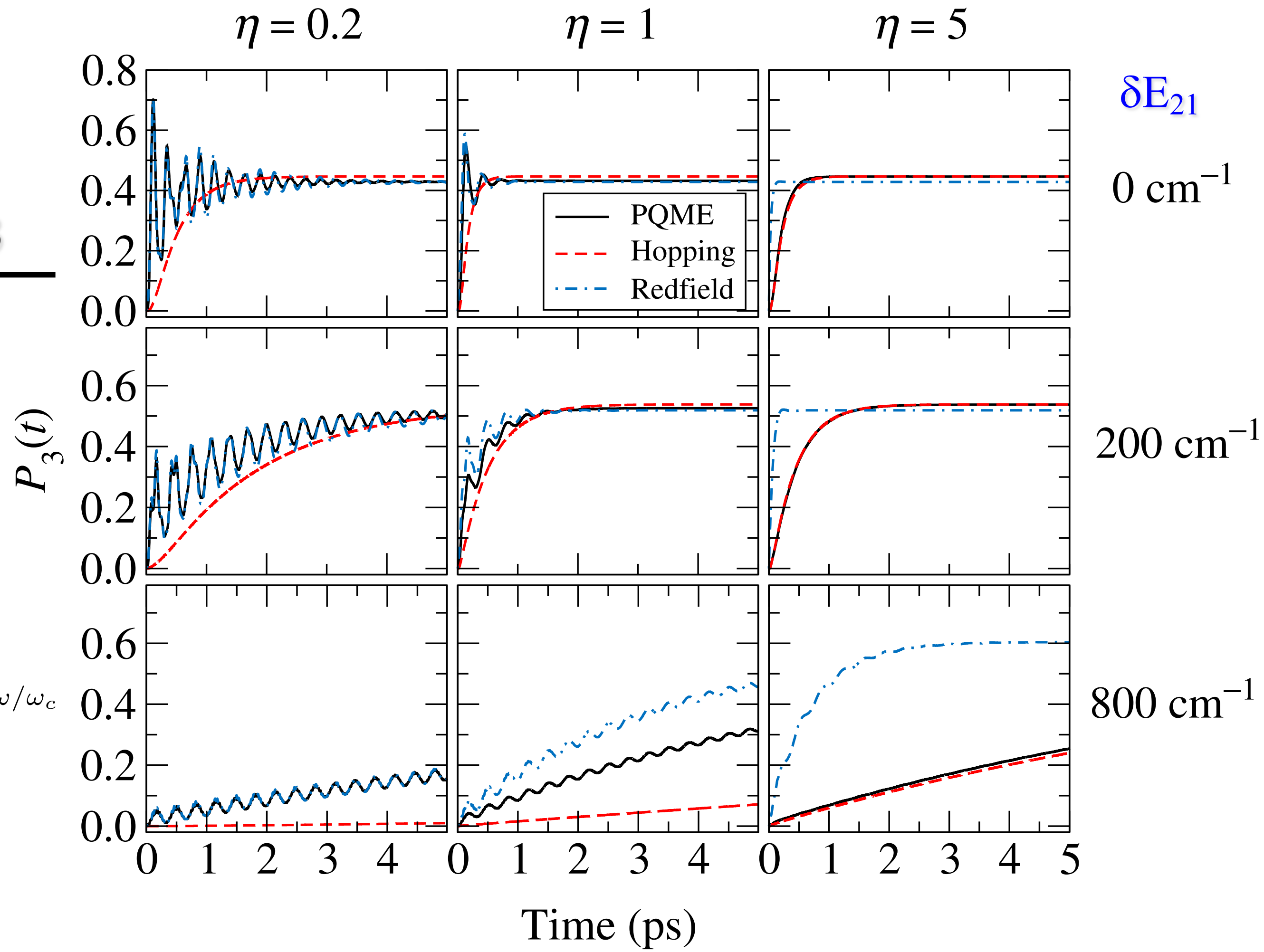
Comparison of PQME with Redfield and Hopping Dynamics

T=300 K & $\hbar\omega_c = 200\ \text{cm}^{-1}$



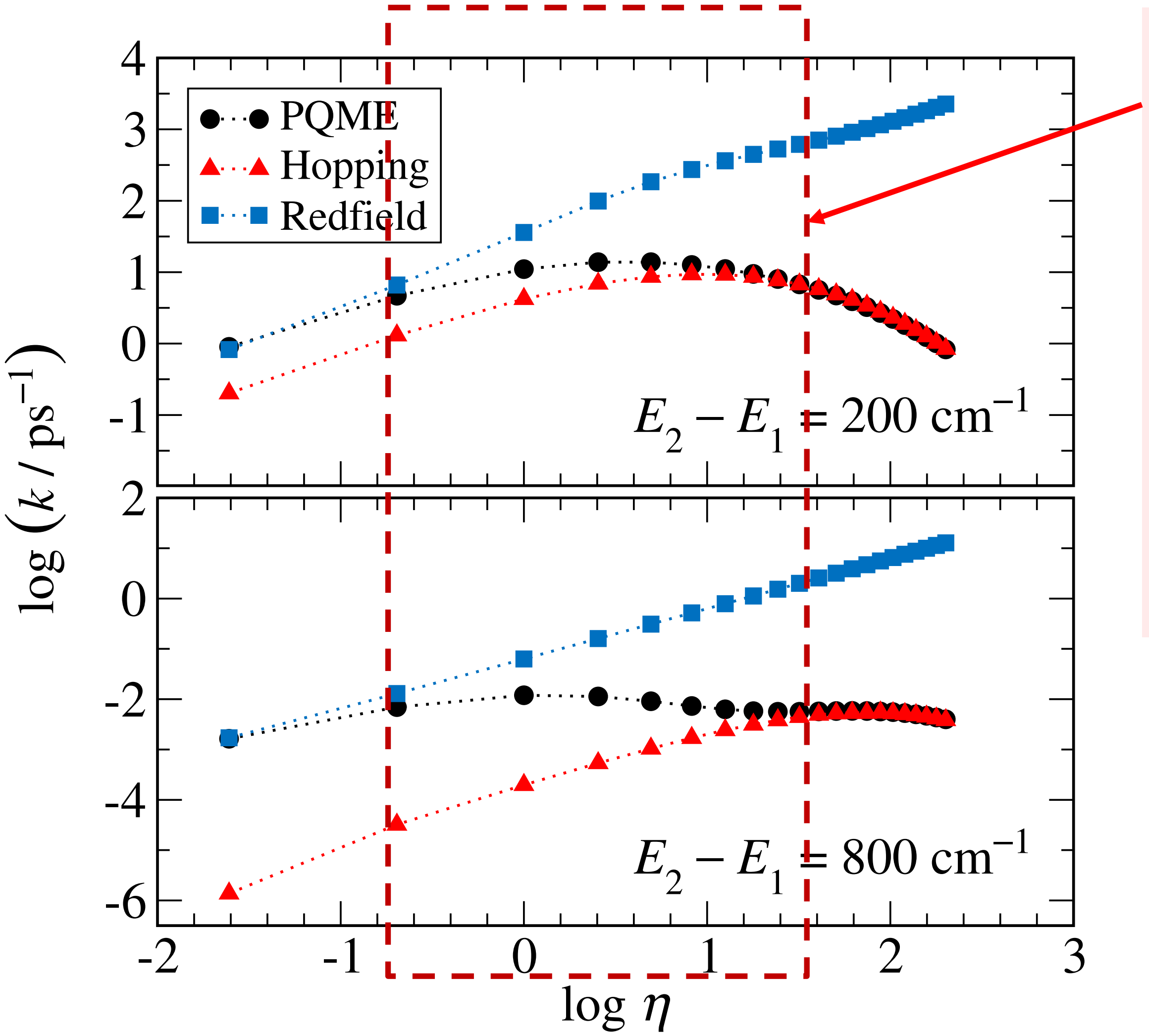
J$_{12}$ =J$_{23}$= 100 cm^{-1}

$$\mathcal{J}_l(\omega) = \sum_n \delta(\omega-\omega_n)\omega_n^2 g_{n,l}^2 = \frac{\eta}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}$$



Jang, Berkelbach, and Reichman, *New. J. Phys.* **15**, 105020 (2013)

Effective rates from PQME for donor-bridge-acceptor model interpolates Redfield (super-exchange) and Hopping dynamics



- Intermediate regime where turn-over occurs is fairly broad.
- Significant interplay of non-adiabatic effects and quantum coherence.

T=300 K &
$\hbar\omega_c = 200\ \mathrm{cm}^{-1}$

Jang, Berkelbach, and Reichman, *New. J. Phys.* **15**, 105020 (2013)

Issues with current version of 2^{nd} order PQME

- Over-relaxation of some slow modes – premature suppression of some coherence terms. Inaccurate for slow bath. [see comprehensive testing in, e.g., C. –K. Lee, J. Moix, and J. Cao, *J. Chem. Phys.* **136**, 204120 (2012)]

- No additional improvement for Ohmic bath and may lead to pathological behavior for sub-Ohmic bath. [This is obvious from vanishing of the Debye-Waller factor.]

- Variational PQME or frozen mode PQME

  D. P. S. McCutcheon and A. Nazir, *J. Chem. Phys.* **135**, 114501 (2011)
  H. -H. Teh, B. –Y. Jin, and Y. –C. Cheng, *J. Chem. Phys.* **150**, 224110 (2019)

Partially polaron transformed QME as a more general framework to address these issues?

Partial polaron transformation

$$H = \sum_{j=1}^{N} E_j |j\rangle\langle j| + \sum_{j,k=1}^{N} J_{jk} |j\rangle\langle k| + \sum_{j=1}^{N}\sum_{n} \hbar\omega_n g_{n,j}(b_n + b_n^\dagger)|j\rangle\langle j| + \sum_{n} \hbar\omega_n (b_n^\dagger b_n + \frac{1}{2})$$

$$\Big\downarrow \qquad G = \sum_{j=1}^{N}\sum_{n} g_{n,j} W_h(\omega_n)(b_n^\dagger - b_n)|j\rangle\langle j|$$

$$W_h(\omega) = \begin{cases} O(\omega^\alpha), & \text{, for } \omega \to 0 \\ 1 & \text{, for } \omega \to \infty \end{cases}$$

$$\tilde{H} = e^G H e^{-G} = \underbrace{\underbrace{\sum_{j=1}^{N} \tilde{E}_j |j\rangle\langle j| + \sum_{j,k=1}^{N} J_{jk} w_{jk} |j\rangle\langle k|}_{\tilde{H}_{0,s}} + H_b}_{\tilde{H}_0}$$

$$+ \underbrace{\sum_{j,k=1}^{N} J_{jk}(\theta_j^\dagger \theta_k - w_{jk})|j\rangle\langle k| + \sum_{j=1}^{N}\sum_{n} \hbar\omega_n g_{n,j}(1 - W_h(\omega_n))(b_n + b_n^\dagger)|j\rangle\langle j|}_{\tilde{H}_1}$$

$$\tilde{E}_j = E_j - \sum_n \hbar\omega_n g_{n,j}^2 W_h(\omega_n)(2 - W_h(\omega_n))$$

$$\theta_j^\dagger \theta_k = e^{\sum_n (g_{n,j} - g_{n,k}) W_h(\omega_n)(b_n^\dagger - b_n)} = e^{\sum_n \delta g_{n,jk} W_h(\omega_n)(b_n^\dagger - b_n)}$$

$$w_{jk} = \langle \theta_j^\dagger \theta_k \rangle = \langle \theta_k^\dagger \theta_j \rangle = e^{-\sum_n \coth(\beta\hbar\omega_n/2)\delta g_{n,jk}^2 W_h(\omega_n)^2/2}$$

Partially Polaron Transformed QME (p-PQME)

Interaction picture of $\tilde{H}_0$ &Projection operator $\mathcal{P}(\cdot) = \rho_b Tr_b \{(\cdot)\}$

Formally exact p-PQME for $\tilde{\sigma}_I(t) = Tr_b \left\{ e^{i\tilde{H}_0 t/\hbar} e^{G} \rho(t) e^{-G} e^{-i\tilde{H}_0 t/\hbar} \right\}$

Time non-local form

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\int_0^t d\tau Tr_b \left\{ \tilde{\mathcal{L}}_{1,I}(t) e_{(+)}^{-i\int_\tau^t d\tau' \mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau')} \mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)\rho_b \right\} \tilde{\sigma}_I(\tau)$$
$$- iTr_b\{\tilde{\mathcal{L}}_{1,I}(t) e_{(+)}^{-i\int_0^t d\tau \mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)} \mathcal{Q}\tilde{\rho}(0)\}$$

$\tilde{\mathcal{L}}_{1,I}(\cdot) = \frac{1}{\hbar}[\tilde{H}_{1,I}(t), (\cdot)]$ $\qquad$ $\mathcal{Q}\tilde{\rho}(0) = e^{G}\rho(0)e^{-G} - \rho_b Tr_b\{e^{G}\rho(0)e^{-G}\}$

Conventional second order approximation, higher order, HEOM, or GQME approach can be developed starting from this formally exact equation.

Partially Polaron Transformed QME (p-PQME)

Time local form

F. Shibata and T. Arimitsu, *J. Phys. Soc. Jpn.* ***49***, 891 (1980)

$$\begin{aligned}\frac{d}{dt}\tilde{\sigma}_I(t) = -\int_0^t d\tau Tr_b\Big\{&\tilde{\mathcal{L}}_{1,I}(t)(1+i\Gamma_{1,I}(t))^{-1}\\ &\times e_{(+)}^{-i\int_\tau^t d\tau'\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau'\tilde{\mathcal{L}}_{1,I}(\tau')}\rho_b\Big\}\tilde{\sigma}_I(t)\\ &- i\mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)(1+i\Gamma_{1,I}(t))^{-1}e_{(+)}^{-i\int_0^t d\tau\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)}\mathcal{Q}\tilde{\rho}(0)\end{aligned}$$

$$\Gamma_{1,I}(t) = \int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau'\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau')}\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{P}e_{(-)}^{i\int_\tau^t d\tau'\tilde{\mathcal{L}}_{1,I}(\tau')}$$

Time local form with second order approximation

$$\begin{aligned}\frac{d}{dt}\tilde{\sigma}_I(t) = &-\int_0^t d\tau Tr_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\rho_b\}\tilde{\sigma}_I(t)\\ &- iTr_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}(0)\} - \int_0^t d\tau Tr_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}(0)\}\end{aligned}$$

Time-local second order p-PQME

$$\frac{d}{dt}\tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t)$$

$$\mathcal{R}(t)\tilde{\sigma}_I(t) = \frac{1}{\hbar^2}\sum_{j,k=1}^{N}\sum_{j',k'=1}^{N}\int_0^t d\tau \langle \tilde{B}_{jk}(t)\tilde{B}_{j'k'}(\tau)\rangle [\mathcal{T}_{jk}(t), \mathcal{T}_{j'k'}(\tau)\tilde{\sigma}_I(t)] + \text{H.c.}$$

$$\mathcal{T}_{jk}(t) = e^{i\tilde{H}_{0,s}t/\hbar}|j\rangle\langle k|e^{-i\tilde{H}_{0,s}t/\hbar}$$

$$\langle \tilde{B}_{jk}(t)\tilde{B}_{j'k'}(\tau)\rangle = \underbrace{\tilde{J}_{jk}\tilde{J}_{j'k'}\left(e^{-\mathcal{K}_{jk,j'k'}(t-\tau)} - 1\right)}_{\text{Polaron-transformed part}} + \underbrace{\delta_{jk}\delta_{j'k'}\mathcal{C}_{jj'}(t-\tau)}_{\text{Untransformed part}}$$
$$+ \underbrace{\delta_{jk}\tilde{J}_{j'k'}\mathcal{M}_{j,j'k'}(t-\tau) + \delta_{j'k'}\tilde{J}_{jk}\mathcal{M}_{j',kj}(t-\tau)}_{\text{Cross terms}}$$

$$\mathcal{K}_{jk,j'k'}(t) = \sum_n \delta g_{n,jk}\delta g_{n,j'k'}W_h(\omega_n)^2\left(\coth\left(\frac{\beta\hbar\omega_n}{2}\right)\cos(\omega_n t) - i\sin(\omega_n t)\right)$$

$$\mathcal{M}_{j,j'k'}(t) = \sum_n \hbar\omega_n g_{n,j}\delta g_{n,j'k'}(1 - W_h(\omega_n))W_h(\omega_n)\left(\cos(\omega_n t) - i\coth\left(\frac{\beta\hbar\omega_n}{2}\right)\sin(\omega_n t)\right)$$

$$\mathcal{C}_{jj'}(t) = \sum_n \hbar^2\omega_n^2 g_{n,j}g_{n,j'}(1 - W_h(\omega_n))^2\left(\coth\left(\frac{\beta\hbar\omega_n}{2}\right)\cos(\omega_n t) - i\sin(\omega_n t)\right)$$

S. J. Jang, *J. Chem. Phys.* **157**, 104107 (2022)

Inhomogeneous terms

$$\mathcal{I}_1(t) = -\frac{i}{\hbar}\sum_{j,k=1}^{N}\sum_{j',k'=1}^{N} Tr_b\left\{\tilde{B}_{jk}(t)\delta\tilde{\rho}_{b,j'k'}\right\}\sigma_{j'k'}(0)[\mathcal{T}_{jk}(t),\mathcal{T}_{j'k'}(0)]$$

$$\mathcal{I}_2(t) = -\frac{1}{\hbar^2}\sum_{j,k=1}^{N}\sum_{j',k'=1}^{N}\sum_{j'',k''=1}^{N}\int_0^t d\tau Tr_b\left\{\tilde{B}_{jk}(t)\tilde{B}_{j'k'}(\tau)\delta\tilde{\rho}_{b,j''k''}\right\}$$
$$\times\,\sigma_{j''k''}(0)[\mathcal{T}_{jk}(t),\mathcal{T}_{j'k'}(\tau)\mathcal{T}_{j''k''}(0)] + \mathrm{H.c.}$$

$$Tr_b\{\tilde{B}_{jk}(t)\delta\tilde{\rho}_{b,j'k'}\} = w_{j'k'}\left\{\tilde{J}_{jk}\left(e^{-\mathcal{K}_{jk,j'k'}(t)}f_{jk,k'}(t)-1\right)+\delta_{jk}\left(\mathcal{M}_{j,j'k'}(t)+h_{j,k'}(t)\right)\right\},$$

$$f_{jk,k'}(t) = \exp\left\{2i\sum_n g_{n,k'}\delta g_{n,jk}W_h(\omega_n)^2\sin(\omega_n t)\right\}$$

$$h_{j,k'}(t) = 2\sum_n \hbar\omega_n g_{n,j}g_{n,k'}(1-W_h(\omega_n))W_h(\omega_n)\cos(\omega_n t)$$

A closed form expression for $Tr_b\left\{\tilde{B}_{jk}(t)\tilde{B}_{j'k'}(\tau)\delta\tilde{\rho}_{b,j''k''}\right\}$ involves $\mathcal{K}_{jk,j'k'}(t), \mathcal{M}_{j,j'k'}(t), \mathcal{C}_{jj'}(t), f_{jk,k'}(t), \&\ h_{j,k'}(t)$

S. J. Jang, *J. Chem. Phys.* **157**, 104107 (2022)

Two-level system coupled to the same type of local-bath (Spin-boson Hamiltonian without common modes)

$$\tilde{H}_0 = \tilde{E}_1|1\rangle\langle 1| + \tilde{E}_2|2\rangle\langle 2| + Jw(|1\rangle\langle 2| + |2\rangle\langle 1|) + \sum_n \hbar\omega_n \left(b_n^\dagger b_n + \frac{1}{2}\right) \quad ,$$

$$\tilde{H}_1 = \sum_n \hbar\omega_n(1 - W_h(\omega_n))(b_n + b_n^\dagger)\left(g_{n,1}|1\rangle\langle 1| + g_{n,2}|2\rangle\langle 2|\right)$$
$$+ J\left\{(\theta - w)|1\rangle\langle 2| + (\theta^\dagger - w)|2\rangle\langle 1|\right\}$$

$$\theta = e^{\sum_n W_h(\omega_n)(g_{n,1} - g_{n,2})(b_n^\dagger - b_n)} \qquad w = \langle\theta\rangle = \langle\theta^\dagger\rangle$$

Calculation of $\mathcal{R}(t)$ involves only the following three correlation functions:

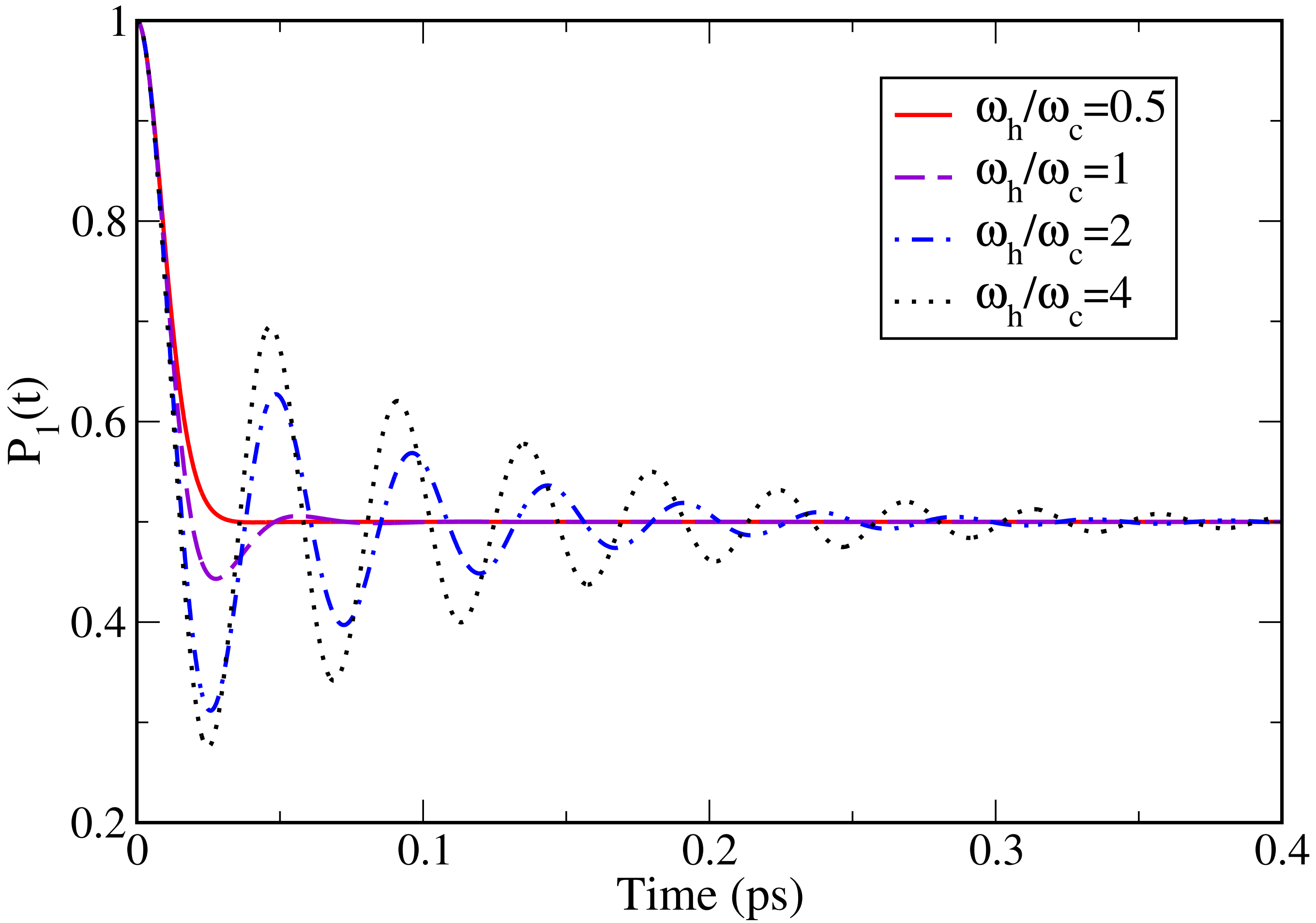
$$\mathcal{K}(t) = \frac{2}{\pi\hbar}\int_0^\infty d\omega \frac{\mathcal{J}(\omega)}{\omega^2} W_h(\omega)^2 \left(\coth\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega t) - i\sin(\omega t)\right)$$

$$\mathcal{M}(t) = \frac{1}{\pi}\int_0^\infty d\omega \frac{\mathcal{J}(\omega)}{\omega} W_h(\omega)(1 - W_h(\omega)) \left(\cos(\omega t) - i\coth\left(\frac{\beta\hbar\omega}{2}\right)\sin(\omega t)\right)$$

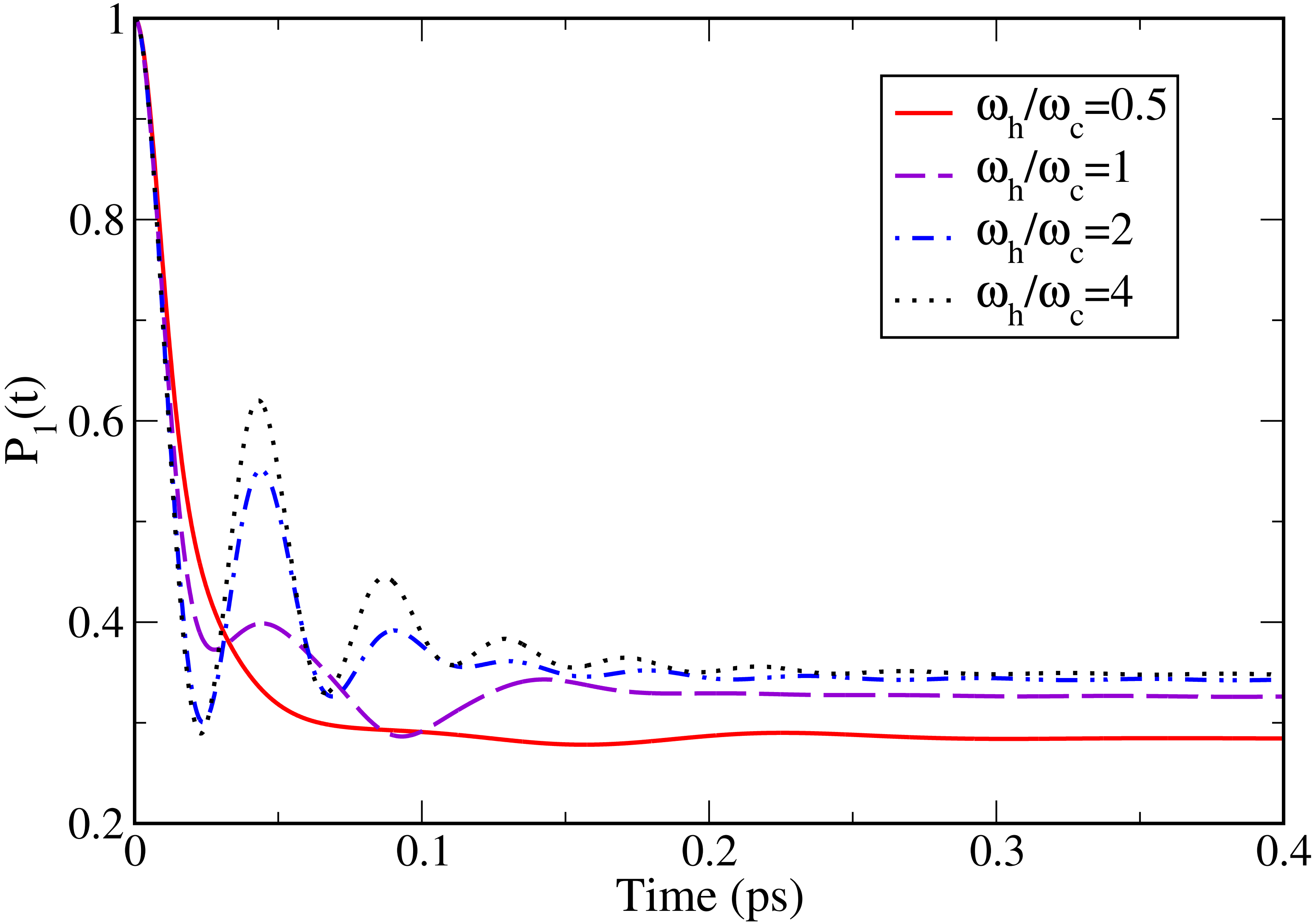
$$\mathcal{C}(t) = \frac{\hbar}{\pi}\int_0^\infty d\omega \mathcal{J}(\omega)(1 - W_h(\omega))^2 \left(\coth\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega t) - i\sin(\omega t)\right)$$

$$\mathcal{J}(\omega) = \pi\hbar\sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n,1}^2 = \pi\hbar\sum_n \delta(\omega - \omega_n)\omega_n^2 g_{n,2}^2$$

S. J. Jang, *J. Chem. Phys.* **157**, 104107 (2022)



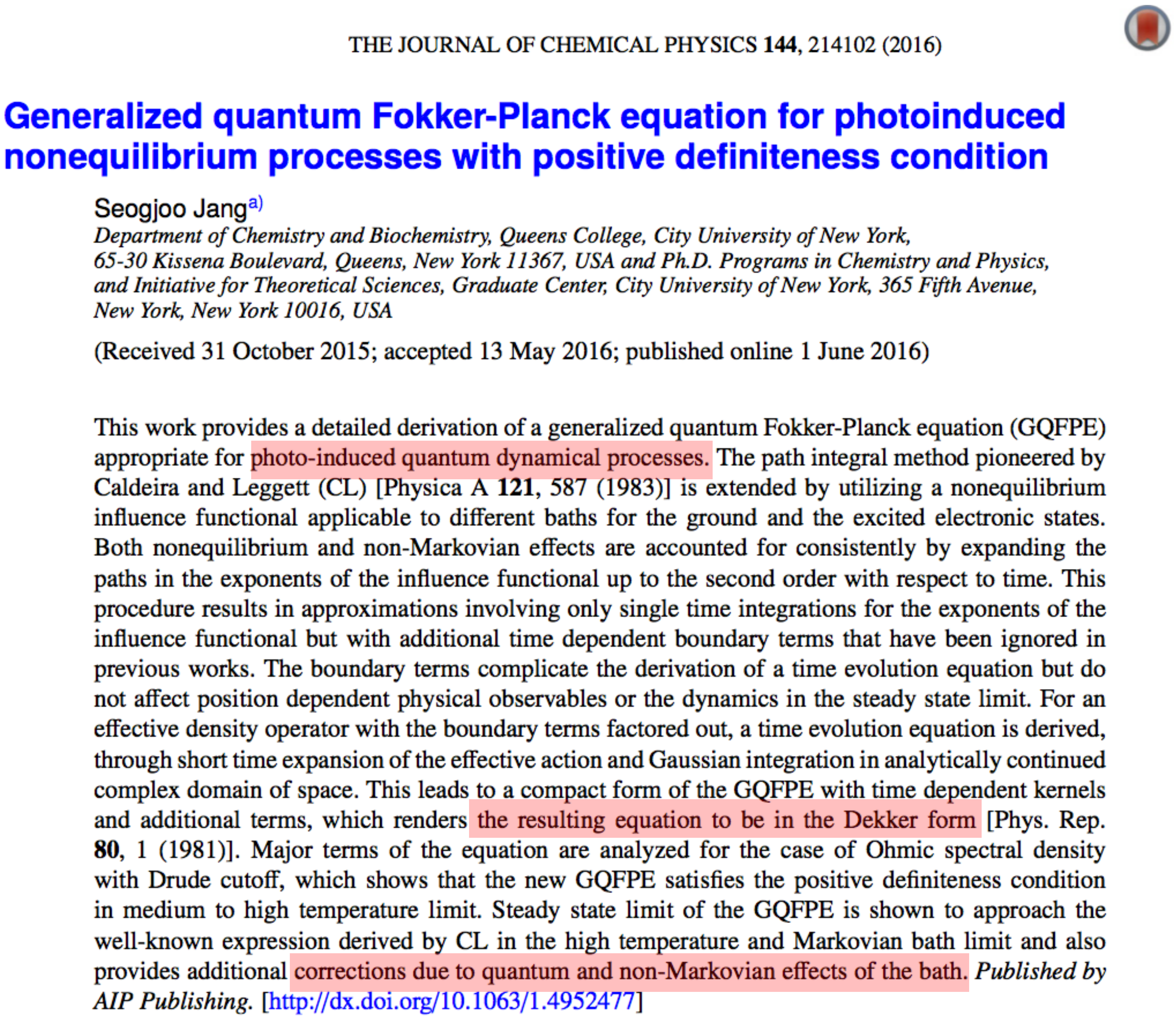
$$E_1 = E_2 \;\&,\; W_h = 1 - \exp\left\{-\left(\omega/\omega_h\right)^2\right\}$$



$$E_1 = E_2 + 200 \text{ cm}^{-1} \;\&,\; W_h = 1 - \exp\left\{-\left(\omega/\omega_h\right)^2\right\}$$

PQME: Summary and Future Direction

- Formally exact QMEs and polaron-transformed QME (PQME).
- PQME, with time dependent relaxation super-operator and inhomogeneous terms, works well in both weak and strong coupling to bath.
- General p-PQME applicable to broad range of open system quantum dynamics including exciton and charge transport dynamics
- Weighting function and its parameters can be used to find the best 2nd order approximation
- Potential applications to quantum information processing and sensing
- Extension to time dependent polaron transformation approach is feasible



THE JOURNAL OF CHEMICAL PHYSICS **144**, 214102 (2016)

Generalized quantum Fokker-Planck equation for photoinduced nonequilibrium processes with positive definiteness condition

Seogjoo Jang[a)]

Department of Chemistry and Biochemistry, Queens College, City University of New York,
65-30 Kissena Boulevard, Queens, New York 11367, USA and Ph.D. Programs in Chemistry and Physics,
and Initiative for Theoretical Sciences, Graduate Center, City University of New York, 365 Fifth Avenue,
New York, New York 10016, USA

(Received 31 October 2015; accepted 13 May 2016; published online 1 June 2016)

This work provides a detailed derivation of a generalized quantum Fokker-Planck equation (GQFPE) appropriate for photo-induced quantum dynamical processes. The path integral method pioneered by Caldeira and Leggett (CL) [Physica A **121**, 587 (1983)] is extended by utilizing a nonequilibrium influence functional applicable to different baths for the ground and the excited electronic states. Both nonequilibrium and non-Markovian effects are accounted for consistently by expanding the paths in the exponents of the influence functional up to the second order with respect to time. This procedure results in approximations involving only single time integrations for the exponents of the influence functional but with additional time dependent boundary terms that have been ignored in previous works. The boundary terms complicate the derivation of a time evolution equation but do not affect position dependent physical observables or the dynamics in the steady state limit. For an effective density operator with the boundary terms factored out, a time evolution equation is derived, through short time expansion of the effective action and Gaussian integration in analytically continued complex domain of space. This leads to a compact form of the GQFPE with time dependent kernels and additional terms, which renders the resulting equation to be in the Dekker form [Phys. Rep. **80**, 1 (1981)]. Major terms of the equation are analyzed for the case of Ohmic spectral density with Drude cutoff, which shows that the new GQFPE satisfies the positive definiteness condition in medium to high temperature limit. Steady state limit of the GQFPE is shown to approach the well-known expression derived by CL in the high temperature and Markovian bath limit and also provides additional corrections due to quantum and non-Markovian effects of the bath. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4952477]

Caldiera and Leggett (CL) QME & QFPE

$$H = \frac{p^2}{2m} + V(q) + \sum_\alpha \left\{ \frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} \left(x_\alpha - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} q \right)^2 \right\}$$

Caldeira and Leggett, *Physica A* **121**, 587 (1983):

Feynman-Vernon influence functional formalism

$$\mathcal{J}(\omega) = \frac{\pi}{2} \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \delta(\omega - \omega_\alpha) = \eta \omega \Theta(\omega/\omega_c)$$

$$\begin{aligned} \mathcal{C}(t) &= \frac{1}{\pi} \int_0^\infty d\omega \mathcal{J}(\omega) \left(\coth(\frac{\beta \hbar \omega}{2}) \cos(\omega t) - i \sin(\omega t) \right) \\ &= \eta \frac{1}{\pi} \int_0^\infty d\omega \ \omega \Theta(\omega/\omega_c) \left(\coth(\frac{\beta \hbar \omega}{2}) \cos(\omega t) - i \sin(\omega t) \right) \\ &\approx \eta \frac{1}{\pi} \int_0^\infty d\omega \ \omega \Theta(\omega/\omega_c) \left(\frac{2}{\beta \hbar \omega} \cos(\omega) - i \sin(\omega t) \right) = \frac{2\eta}{\beta \hbar} \tilde{\delta}_{\omega_c}(t) - i \tilde{\delta}'_{\omega_c}(t) \end{aligned}$$

$\Theta(\omega/\omega_c)$: Cutoff function decaying faster than ω_c/ω (ω_c : cutoff frequency)

- Short time expansion of the influence functional
- High temperature and Markovian approximation

$$\lim_{\omega_c \to \infty} \tilde{\delta}_{\omega_c}(t) = \delta(t) \ \& \ \lim_{\omega_c \to \infty} \tilde{\delta}'_{\omega_c}(t) = \delta'(t)$$

Caldeira and Leggett (CL) QME

$$\frac{d}{dt}\sigma(t) = -\frac{i}{\hbar}\left[\frac{p^2}{2m} + V(q), \sigma(t)\right] - \frac{\eta}{\beta\hbar^2}\Big[q, \big[q, \sigma(t)\big]\Big] - \frac{i\eta}{2\hbar m}\Big[q, \big\{p, \sigma(t)\big\}\Big]$$

$$W(q,p,t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dy\ \sigma(q - \frac{y}{2}, q + \frac{y}{2}, t)e^{ipy/\hbar}$$

CL Quantum Fokker-Planck Equation (CL-QFPE)

$$\frac{\partial}{\partial t}W(q,p,t) = \left\{-\frac{p}{m}\frac{\partial}{\partial q} + (V'(q) - \hat{F}_Q)\frac{\partial}{\partial p} + \frac{\eta}{m}\frac{\partial}{\partial p}p + \eta k_B T\frac{\partial^2}{\partial p^2}\right\}W(q,p,t)$$

Quantum Force: $\hat{F}_Q = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}\hbar^{2n}}{2^{2n}(2n+1)!}V^{(2n+1)}(q)\frac{\partial^{2n}}{\partial p^{2n}}$

Issues with CL-QME or CL-QFPE

- Non-positive definite - can lead to negative probability for certain initial condition.
- Application of both high temperature limit and Markovian approximation may not be well defined.

$$\frac{1}{\text{time scale of system}} << \omega_c << \frac{k_B T}{\hbar} (\sim 4 \times 10^{13} s^{-1} \text{ at } 300 \text{ K})$$

CL-QME or CL-QFPE is in fact identical to the second order QME in the high temperature Markovian bath limit, which suffers from the same issue.

Correction and Extension of CL-QFPE

- L. Diosi [*Physica A* **199**, 517 (1993)]: QFPE in Dekker-Form (a kind of Lindblad Eqn. satisfying translational invariance) for intermediate temperature regime – Derived from a kind of cumulant approximation with neglect of initial non-equilibrium relaxation

- Ankerhold, Pechukas, and Grabert [*Phys. Rev. Lett. 87*, 086802 (2001)]: Quantum Smoluchowski Equation for the diagonal elements (in position space) of the reduced density operator, Strong friction and Markovian bath limit. – Strong coupling limit of influence functional formalism

QME in the Dekker-Form

$$\hat{\tilde{\sigma}}_e(q_g(\cdot);t) = \int dq' \int dq'' |q'\rangle \tilde{\sigma}_e(q',q'',q_g(\cdot);t)\langle q''|$$

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\tilde{\sigma}}_e(q_g(\cdot);t) = -\frac{i}{\hbar}[\hat{H}_{eff}(t),\hat{\tilde{\sigma}}_e] - \frac{i}{\hbar}\frac{\tilde{\mathcal{K}}_I^{(1)}(t)}{m_e(t)}\left[\hat{q},\{\hat{p},\hat{\tilde{\sigma}}_e\}\right] \\ +\frac{1}{\hbar}\left(\frac{\tilde{\mathcal{K}}_R^{(1)}(t)}{m_e(t)} - 2\frac{\mathcal{K}_R^{(2)}(t)}{m_e(t)^2}\tilde{\mathcal{K}}_I^{(1)}(t)\right)\boxed{\left[\hat{q},[\hat{p},\hat{\tilde{\sigma}}_e]\right]} \\ -\frac{\alpha(t)}{\hbar}\left[\hat{q},[\hat{q},\hat{\tilde{\sigma}}_e]\right] - \frac{\mathcal{K}_R^{(2)}(t)}{2\hbar m_e(t)^2}\boxed{\left[\hat{p},[\hat{p},\hat{\tilde{\sigma}}_e]\right]}\end{aligned}$$

Terms missing in CL-QME

$$\hat{H}_{eff}(t) = \frac{\hat{p}^2}{2m_e(t)} + U_e(\hat{q},q_g(\cdot),t)$$

$$U_e(q,q_g(\cdot),t) = V_e(q) + \left(\frac{\kappa_e}{2} - \mathcal{K}_I^{(0)}(t)\right)q^2 - \tilde{\eta}_c(t,q_g(\cdot))q$$

QME for Drude spectral density of bath

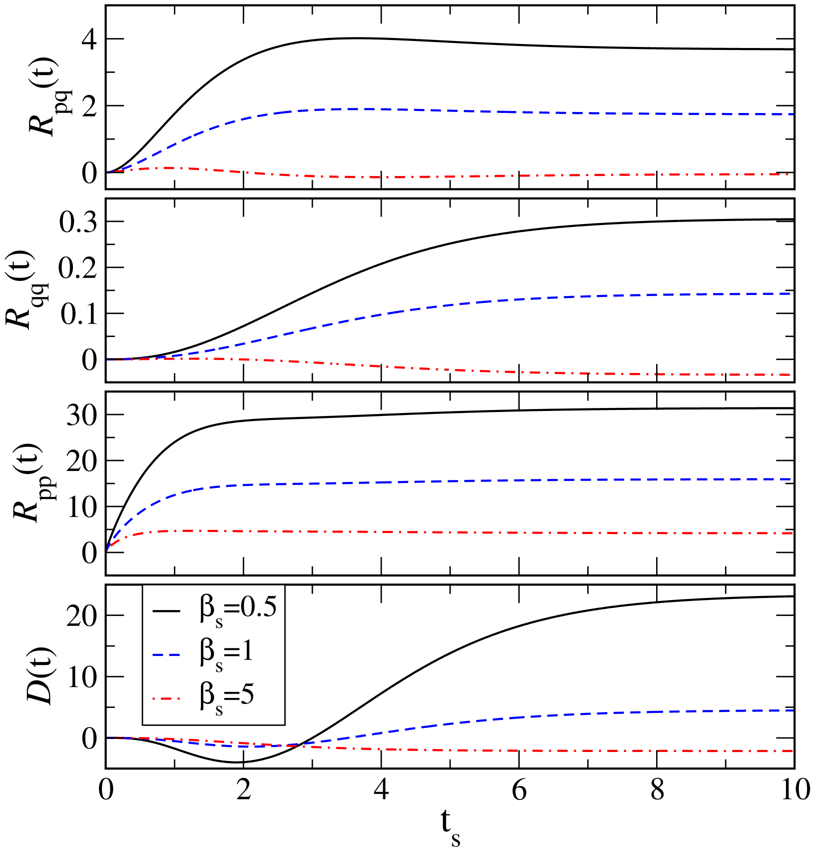
$$\boxed{\eta_e(\omega) = \eta \frac{\omega_c^2 \omega}{\omega^2 + \omega_c^2} = 2m\gamma_e \frac{\omega_c^2 \omega}{\omega^2 + \omega_c^2}}$$

$$\frac{\partial}{\partial t}\hat{\tilde{\sigma}}_e(q_g(\cdot);t) = -\frac{i}{\hbar}[\hat{H}_{eff}(t), \hat{\tilde{\sigma}}_e] - \frac{m\gamma_e^2}{\hbar}\mathcal{R}_{pp}(t)\left[\hat{q}, [\hat{q}, \hat{\tilde{\sigma}}_e]\right] - \frac{i\gamma_e}{\hbar}\Gamma(t)\left[\hat{q}, \{\hat{p}, \hat{\tilde{\sigma}}_e\}\right]$$
$$+\frac{\gamma_e}{\hbar}\mathcal{R}_{pq}(t)\left[\hat{q}, [\hat{p}, \hat{\tilde{\sigma}}_e]\right] - \frac{\mathcal{R}_{qq}(t)}{m\hbar}\left[\hat{p}, [\hat{p}, \hat{\tilde{\sigma}}_e]\right]$$

Positivity Condition,

$$D(t) \equiv 4\mathcal{R}_{pp}(t)\mathcal{R}_{qq}(t) - \mathcal{R}_{pq}(t)^2 - \Gamma(t)^2 > 0$$

is satisfied for high and intermediate temperature regime.



$$\beta_s = \beta\hbar\omega_c = \frac{\hbar\omega_c}{k_B T}$$

$$t_s = t\omega_c$$

$$\frac{\gamma_e}{\omega_c} = 0.1$$

QFPE for Wigner Distribution

$$W(q,p,t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dy\ \tilde{\sigma}_e(q-\frac{y}{2}, q+\frac{y}{2}, t)e^{ipy/\hbar}$$

$$\begin{aligned}\frac{\partial}{\partial t}W(q,p,t) = \Bigg\{ & -\frac{p}{m_e(t)}\frac{\partial}{\partial q} + (V'(q) - \hat{F}_Q)\frac{\partial}{\partial p} + 2m\gamma_e\omega_c e^{-\omega_c t} q\frac{\partial}{\partial p} \\ & -\tilde{\eta}_c(t, q_g(\cdot))\frac{\partial}{\partial p} + 2\gamma_e\Gamma(t)\frac{\partial}{\partial p}p + m\gamma_e^2\hbar\mathcal{R}_{pp}(t)\frac{\partial^2}{\partial p^2} \\ & +\hbar\gamma_e\mathcal{R}_{pq}(t)\frac{\partial^2}{\partial p\partial q} + \frac{\hbar}{m}\mathcal{R}_{qq}(t)\frac{\partial^2}{\partial q^2}\Bigg\} W(q,p,t)\end{aligned}$$

Quantum Force: $\hat{F}_Q = \sum_{n=1}^{\infty}\frac{(-1)^{n-1}\hbar^{2n}}{2^{2n}(2n+1)!}V^{(2n+1)}(q)\frac{\partial^{2n}}{\partial p^{2n}}$

QFPE in the steady state & at intermediate/high temperature

For $e^{-\omega_c t} \approx 0, \tilde{\eta}_c(t, q_g(\cdot)) \approx 0,$ and $\beta\hbar\omega_c << 1$

$$\frac{\partial}{\partial t} W(q,p,t) = \left\{ -\frac{p}{m_{e,s}} \frac{\partial}{\partial q} + \left(V'(q) - \hat{F}_Q \right) \frac{\partial}{\partial p} + A \frac{\partial}{\partial p} p + D_p \frac{\partial^2}{\partial p^2} \right. \\ \left. + B \frac{\partial^2}{\partial p \partial q} + D_q \frac{\partial^2}{\partial q^2} \right\} W(q,p,t) + O((\beta\hbar\omega_c)^2)$$

$$m_{e,s} = 1 - 2\gamma_s, \text{ where } \gamma_s = \gamma_e / \omega_c$$

$$A = \frac{2\gamma_e}{(1 - 2\gamma_s)} = \frac{\eta}{m_{e,s}} \qquad B = 2k_B T \gamma_s \frac{1 - 4\gamma_s}{(1 - 2\gamma_s)^2}$$

$$D_p = 2m\gamma_e k_B T \frac{(1 - 6\gamma_s + 10\gamma_s^2)}{(1 - 2\gamma_s)^2} = \eta k_B T \frac{(1 - 6\gamma_s + 10\gamma_s^2)}{(1 - 2\gamma_s)^2} \qquad D_q = \frac{\gamma_s k_B T}{m\omega_c (1 - 2\gamma_s)^2}$$

A new positive definite QFPE applicable to intermediate couplings and temperature

QFPE: Summary and Future Direction

- Non-positivity of CL-QFPE is an outcome of Markovian approximation
- Inclusion of finite time scale of bath leads to positive definite QFPE, which remains valid except for very low temperature limit
- New generalized QFPE can be applied to both nonequilibrium photoinduced processes and equilibrium quantum dynamics, and well-defined positive definiteness condition clarifies when it can be used
- New correction of CL-QFPE for intermediate coupling and intermediate temperature, which can be used for quantum barrier crossing, quantum thermodynamics including quantum generalization of thermodynamic uncertainty relation.
- Development of Langevin-type equation for new QFPE – allows more general multidimensional quantum simulation in open environments

Overall Summary and Future Direction

- There are important exact relations on quantum estimation and quantum entropy production, but many final expressions applicable to actual systems are based on Lindblad and/or other simplified dynamical equations.

- There is much to understand the effects of non-Markovian open system quantum dynamics, beyond weak system-bath (reservoir) couplings and how these manifest in quantum sensing, which in general involves intermediate to strong interactions with quantum systems.

- Significant progress has been made in developing very accurate open system quantum dynamics methods.

- Further advances and recent efforts to combine Machine Learning approaches will likely to produce quantitatively reliable methods that are generally applicable.