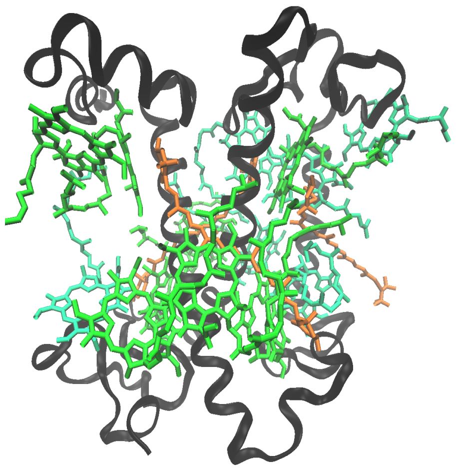
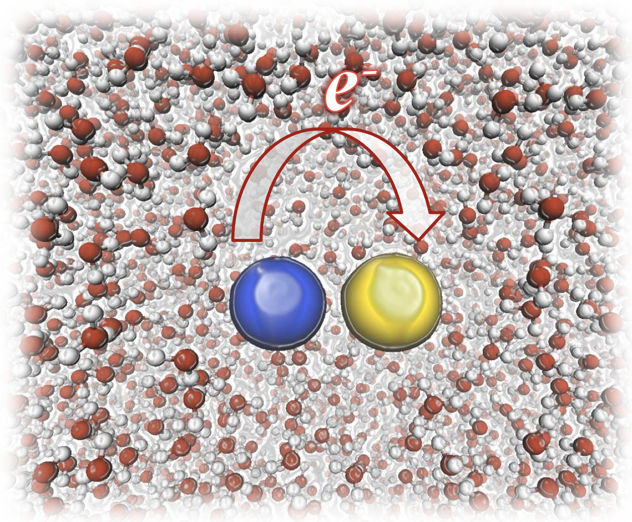
Nonadiabatic Charge and Energy Transfer





Aaron Kelly

Department of Chemistry

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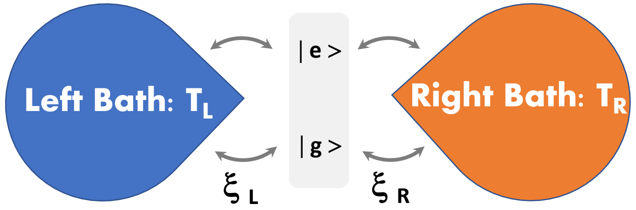

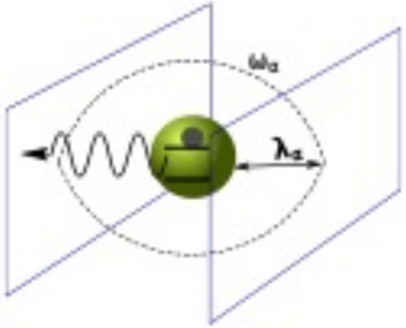

Prof. Dr. Angel Rubio

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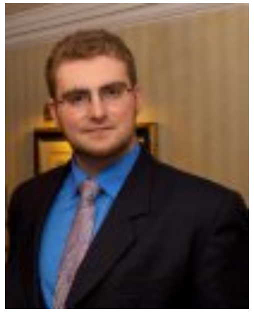

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Dr. Andres Montoya-Castillo

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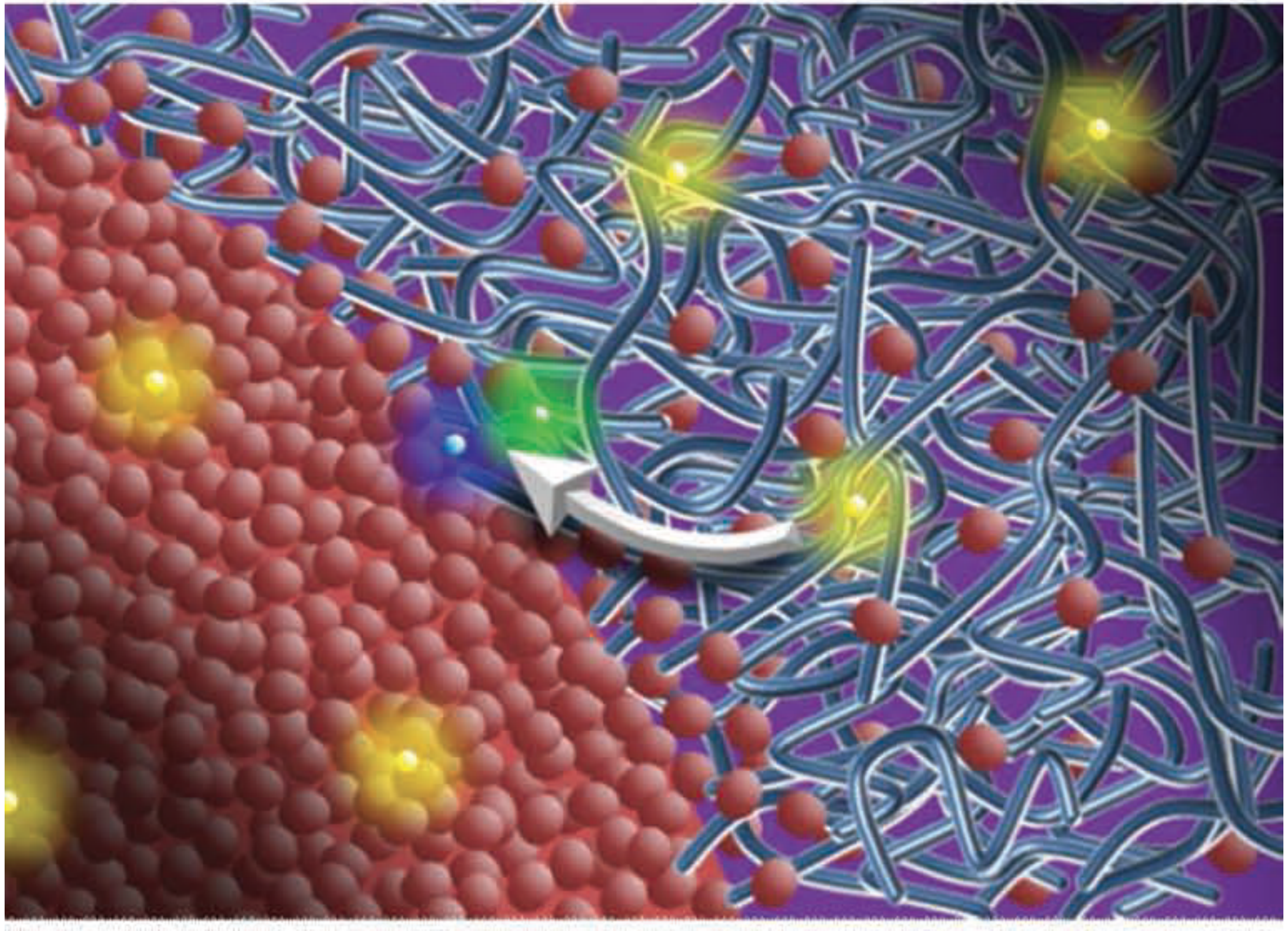
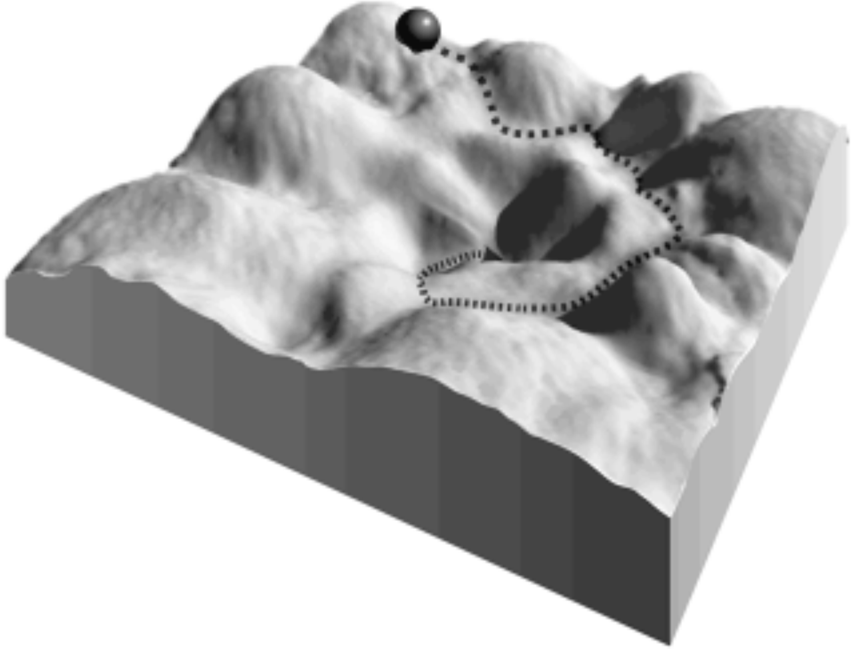
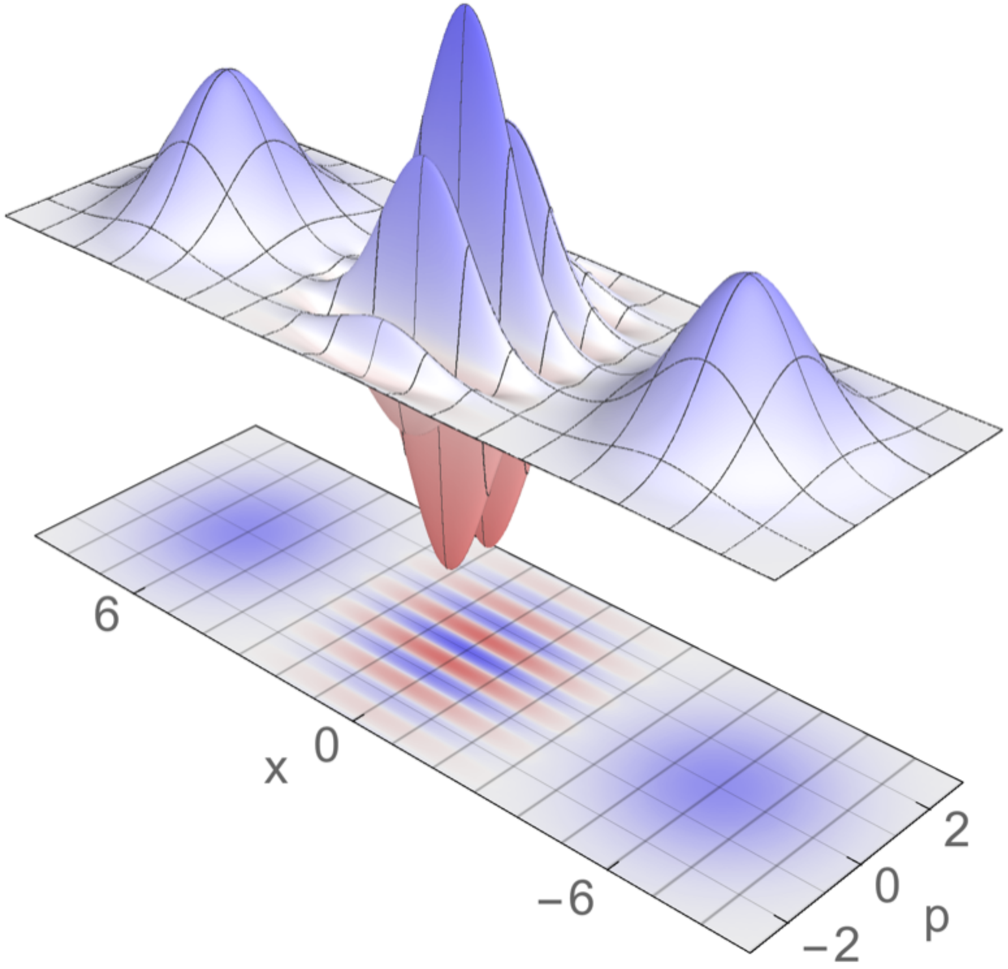
Motivation



Situation





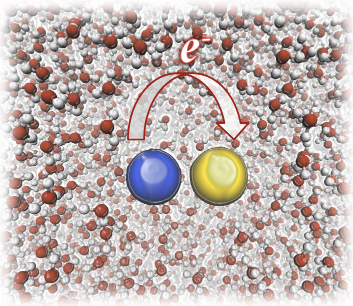
Challenge : $$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$$

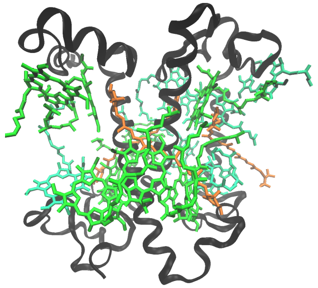
- **High-dimensional (open) systems (nuclei, electrons, photons)**
- **Compatible with both model Hamiltonians and *ab initio* methods.**
- **"Accuracy" in different physical and chemical settings.**
- **Computational cost less than or equal to …**

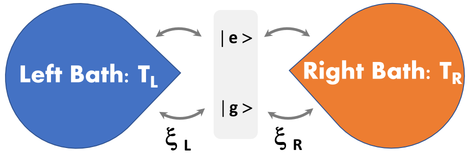
Challenge : $$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$$

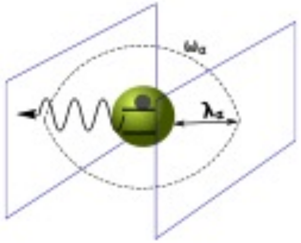
- **High-dimensional systems (nuclei, electrons, photons)**
- **Compatible with both model Hamiltonians and *ab initio* methods.**
- **"Accuracy" in different physical and chemical settings.**
- **Computational cost less than or equal to … MEAN FIELD THEORY.**
- **Systematic improvability would also be nice….**

Outline









- Quantum – classical dynamics and Ehrenfest mean-field theory
- The Nakajima-Zwanzig generalized quantum master equation
- Trajectory-based dynamics methods via wavefunction ansatze

Quantum Dynamics

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]$$

Quantum Dynamics

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]$$

$$\hat{\rho}_W(R,P) = (2\pi\hbar)^{-3N} \int dZ\, e^{iP\cdot Z/\hbar} \langle R - \frac{Z}{2} | \hat{\rho} | R + \frac{Z}{2} \rangle$$

Quantum Dynamics

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$$\left(\hat{A}\hat{B}\right)_W(R,P) = \hat{A}_W(R,P)e^{\hbar\Lambda/2i}\hat{B}_W(R,P)$$

Quantum Dynamics

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$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}\left(\hat{H}_W(R,P)e^{\hbar\Lambda/2i}\hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t)e^{\hbar\Lambda/2i}\hat{H}_W(R,P)\right)$$

Quantum Dynamics

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}\left(\hat{H}_W(R,P)e^{\hbar\Lambda/2i}\hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t)e^{\hbar\Lambda/2i}\hat{H}_W(R,P)\right)$$

$$\mu = (m/M)^{1/2}$$

Quantum Dynamics

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}\left(\hat{H}_W(R,P)e^{\hbar\Lambda/2i}\hat{\rho}_W(R,P,t) - \hat{\rho}_W(R,P,t)e^{\hbar\Lambda/2i}\hat{H}_W(R,P)\right)$$

$$\mu = (m/M)^{1/2}$$

$$\frac{\partial \hat{\rho}'_W(R',P',t')}{\partial t'} = -i(\hat{H}'_W(R',P')e^{\mu\Lambda'/2i}\hat{\rho}'_W(R',P',t') - \hat{\rho}'_W(R',P',t')e^{\mu\Lambda'/2i}\hat{H}'_W(R',P'))$$

Quantum-Classical Dynamics

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\right] + \frac{1}{2}\left(\{\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\} - \{\hat{\rho}_W(R,P,t),\hat{H}_W(R,P)\}\right)$$

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -i\hat{\mathscr{L}}\hat{\rho}_W(R,P,t)$$

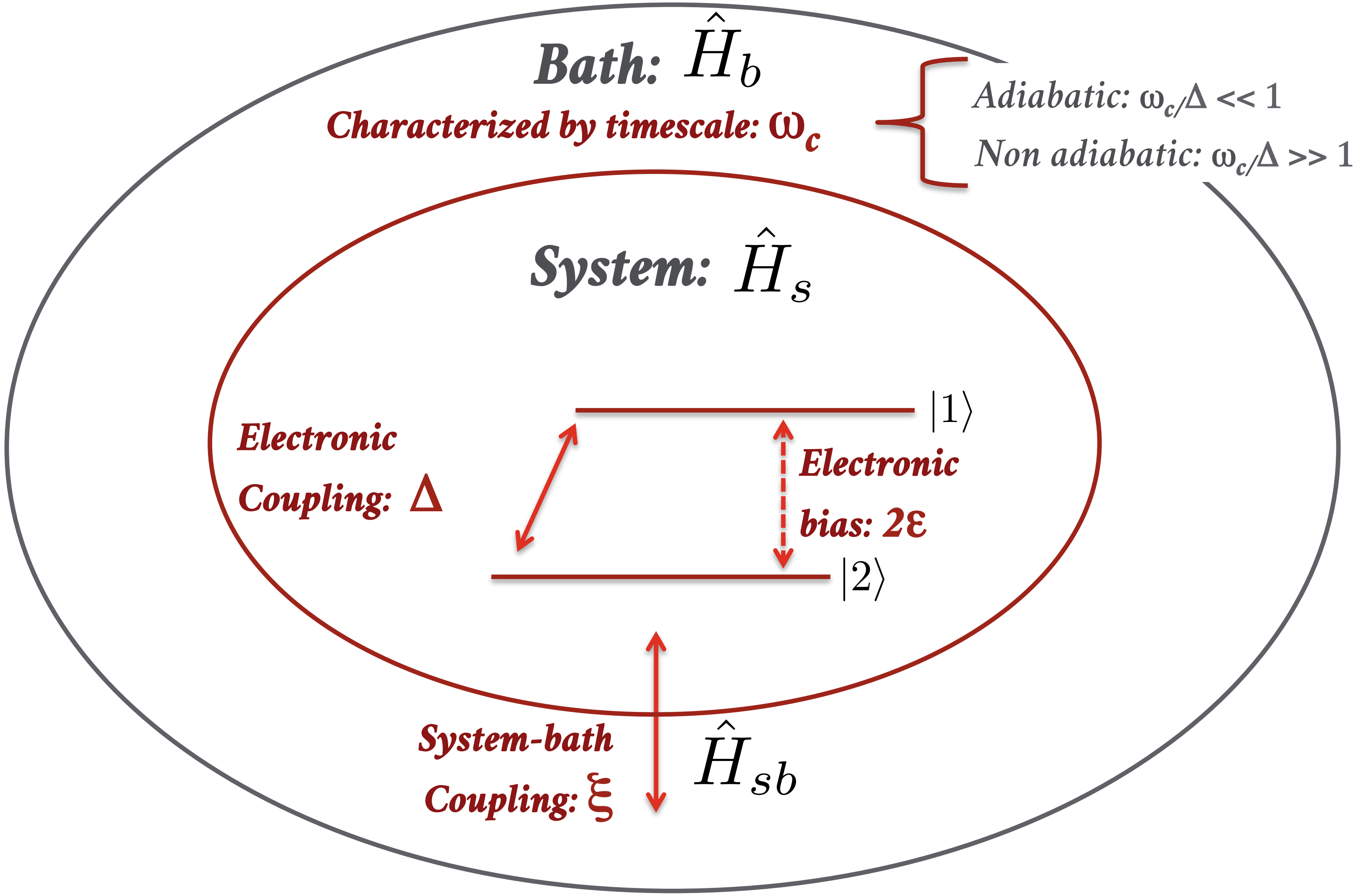
Kapral and Ciccotti, JCP, 1999.

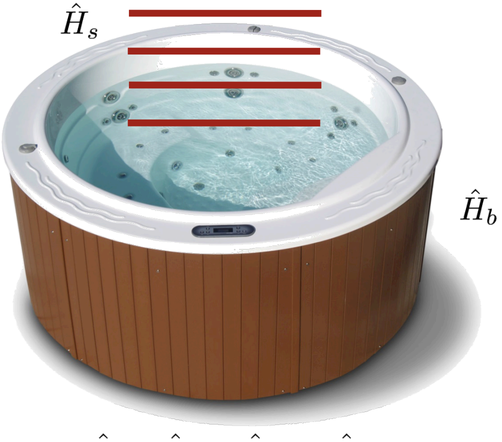
Quantum-Classical Dynamics

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\right] + \frac{1}{2}\left(\{\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\} - \{\hat{\rho}_W(R,P,t),\hat{H}_W(R,P)\}\right)$$

$$\hat{H}_W = H_e(X) + \hat{H}_s(\hat{q}) + \hat{V}_c(\hat{q},R)$$

System-Bath Model





$$\hat{H} = \hat{H}_s + \hat{H}_{sb} + \hat{H}_b$$

Bath Spectral Density

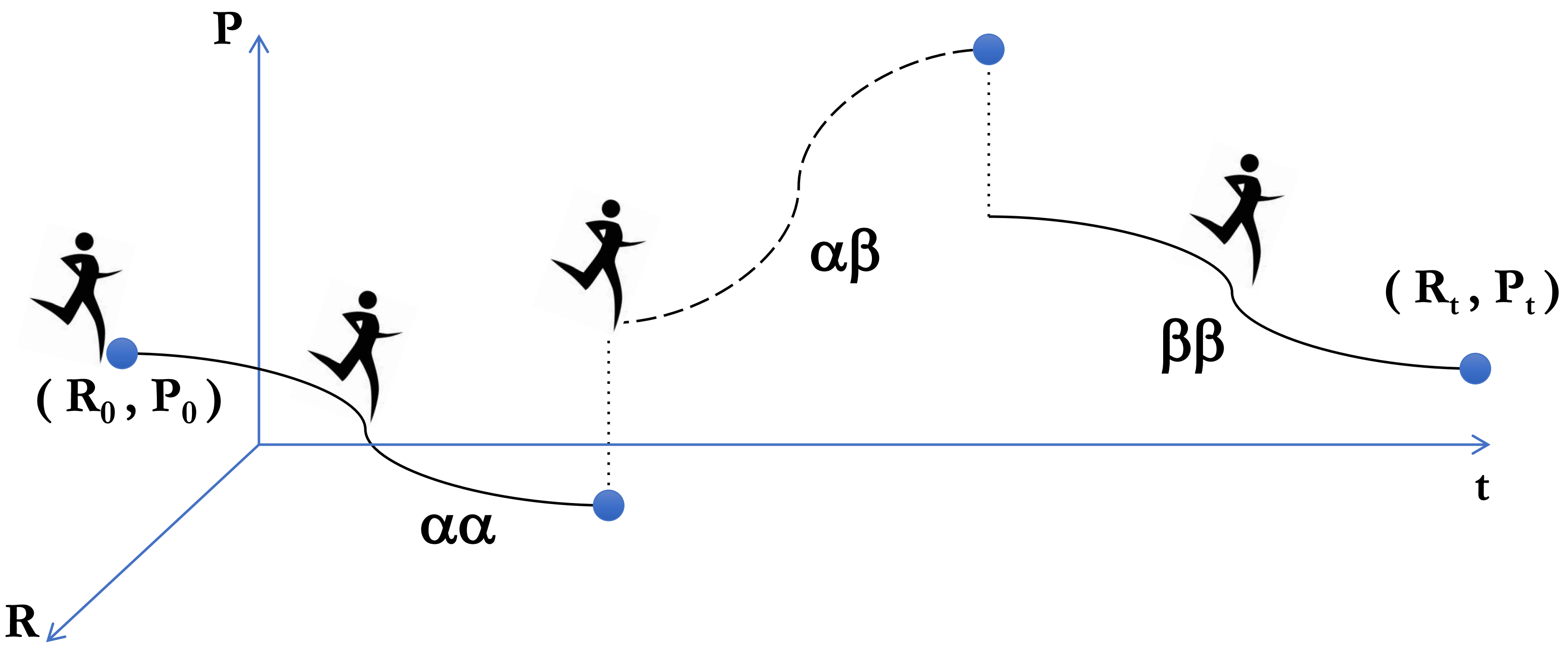
$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j)$$

Spin Boson Hamiltonian:

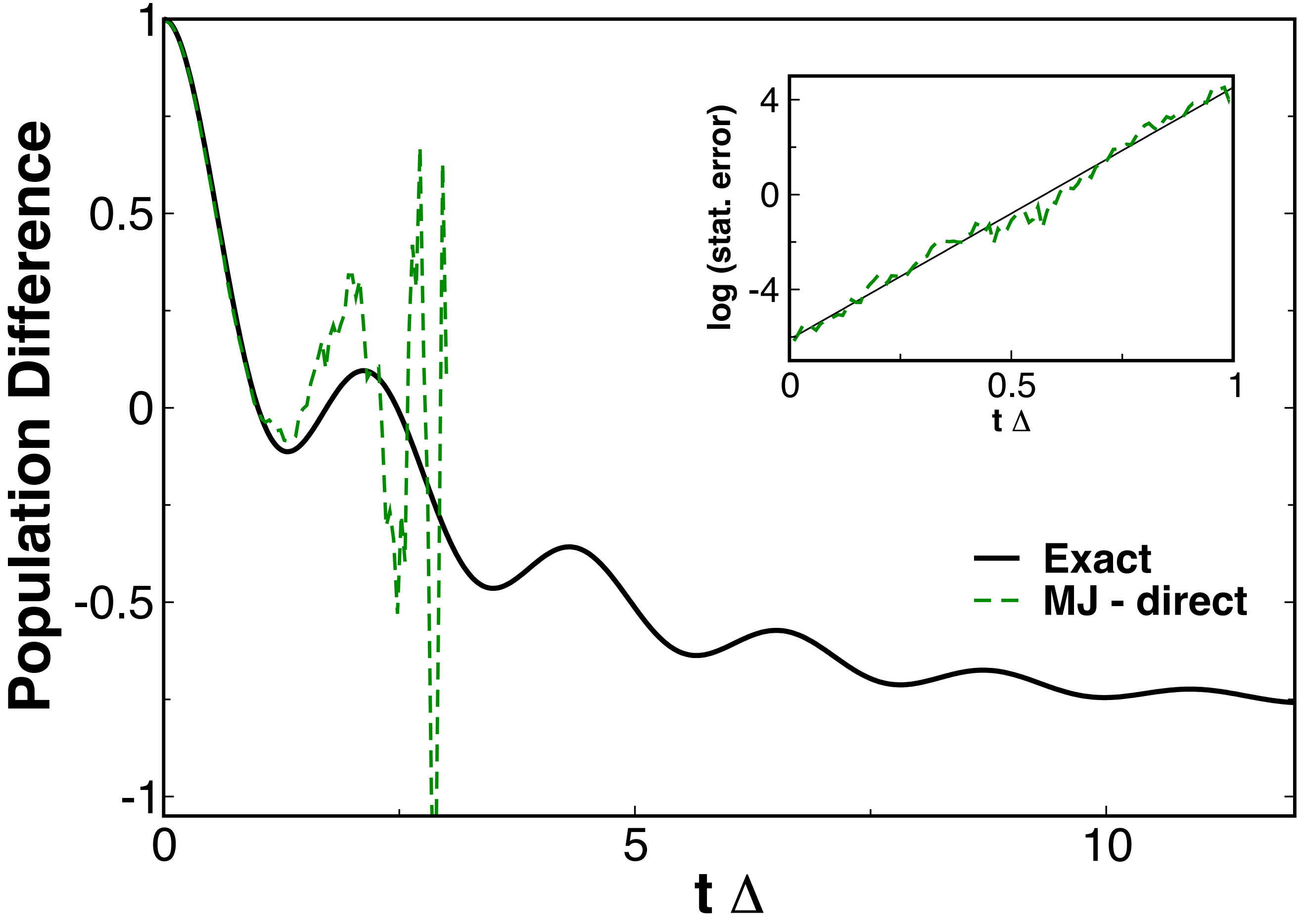
$$\hat{H} = \epsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x + \frac{\hat{P}^2}{2M} + \sum_j \left(\frac{1}{2} M_j \omega_j^2 \hat{R}_j^2 - c_j \hat{R}_j \hat{\sigma}_z \right)$$

Surface Hopping

- A natural choice for trajectory-based simulations is to work in the adiabatic basis, which often leads to surface-hopping type algorithms.
    - e.g. Fewest Switches Surface Hopping (FSSH)
- However, other (more rigorous) surface-hopping schemes are also available
    - e.g. Momentum-jump approximation to the QCLE



QCLE - Surface Hopping



Hierarchy of Trajectory Based Approaches

Cost

Full semiclassical
e.g. SC-IVR, QCLE, ILDM — *A lot!*

Partially linearized
e.g. PLDM, FBTS — *~20x-40x*

Increasing dynamical correlation (and accuracy)

Linearized semiclassical e.g. LSC-IVR, PBME, LAND-map — *~10x*

Mean field theory e.g. Ehrenfest — *1x*

$$\hat{\rho}(t) = \hat{\rho}_s(t)\hat{\rho}_b(t)$$

Mean Field Theory from Quantum-Classical Dynamics

$$\hat{\rho}_s(t) = \int dX\, \hat{\rho}_W(X,t)$$

$$\rho_e(X,t) = \mathrm{Tr}'\hat{\rho}_W(X,t)$$

Mean Field Theory is "Uncorrelated" Quantum-Classical Dynamics

$$\hat{\rho}_s(t) = \int dX \; \hat{\rho}_W(X,t)$$

$$\rho_e(X,t) = \mathrm{Tr}'\hat{\rho}_W(X,t)$$

$$\hat{\rho}_W(X,t) \equiv \hat{\rho}_s(t)\rho_e(X,t) + \hat{\rho}_{cor}(X,t)$$

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Mean Field Theory from Quantum-Classical Dynamics

$$\frac{\partial \rho_e(X,t)}{\partial t} = \left\{ H_e + \mathrm{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X,t) \right\}$$

Mean Field Theory from Quantum-Classical Dynamics

$$\frac{\partial \rho_e(X,t)}{\partial t} = \left\{ H_e + \mathrm{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X,t) \right\}$$

$$\dot{R}(t) = \frac{P(t)}{M}, \quad \dot{P}(t) = -\frac{\partial V_{\mathrm{eff}}(R(t))}{\partial R(t)}.$$

Mean Field Theory from Quantum-Classical Dynamics

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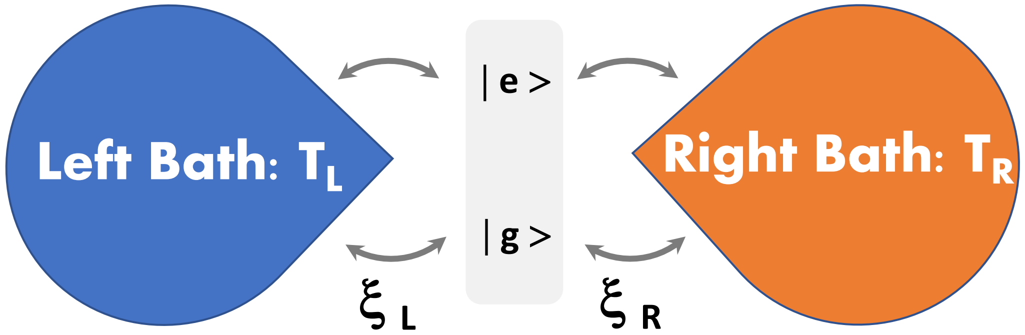
$$\dot{R}(t) = \frac{P(t)}{M}, \quad \dot{P}(t) = -\frac{\partial V_{\mathrm{eff}}(R(t))}{\partial R(t)}.$$

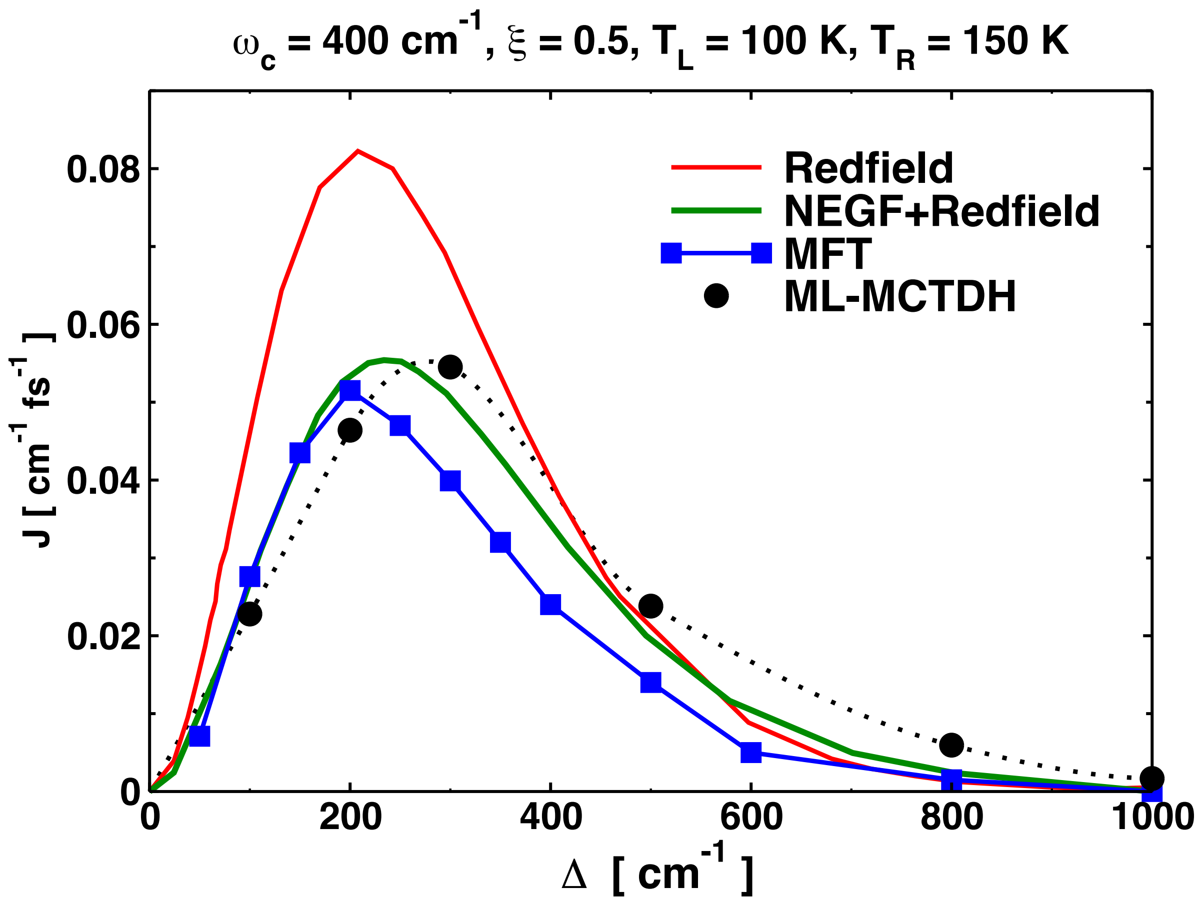
$$\frac{\partial \hat{\rho}_s(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s + \int dX\, \hat{V}_c \rho_e(X,t), \hat{\rho}_s(t) \right]$$

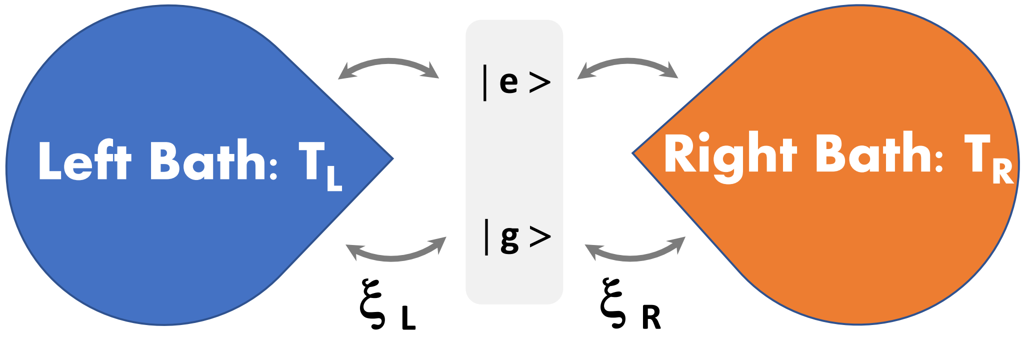
Heat Transport through a Molecular Junction



$$g_\lambda(\omega) = \frac{\pi}{2}\xi_\lambda \omega \exp(-\omega/\omega_{c,\lambda})$$

Heat Transport through a Molecular Junction





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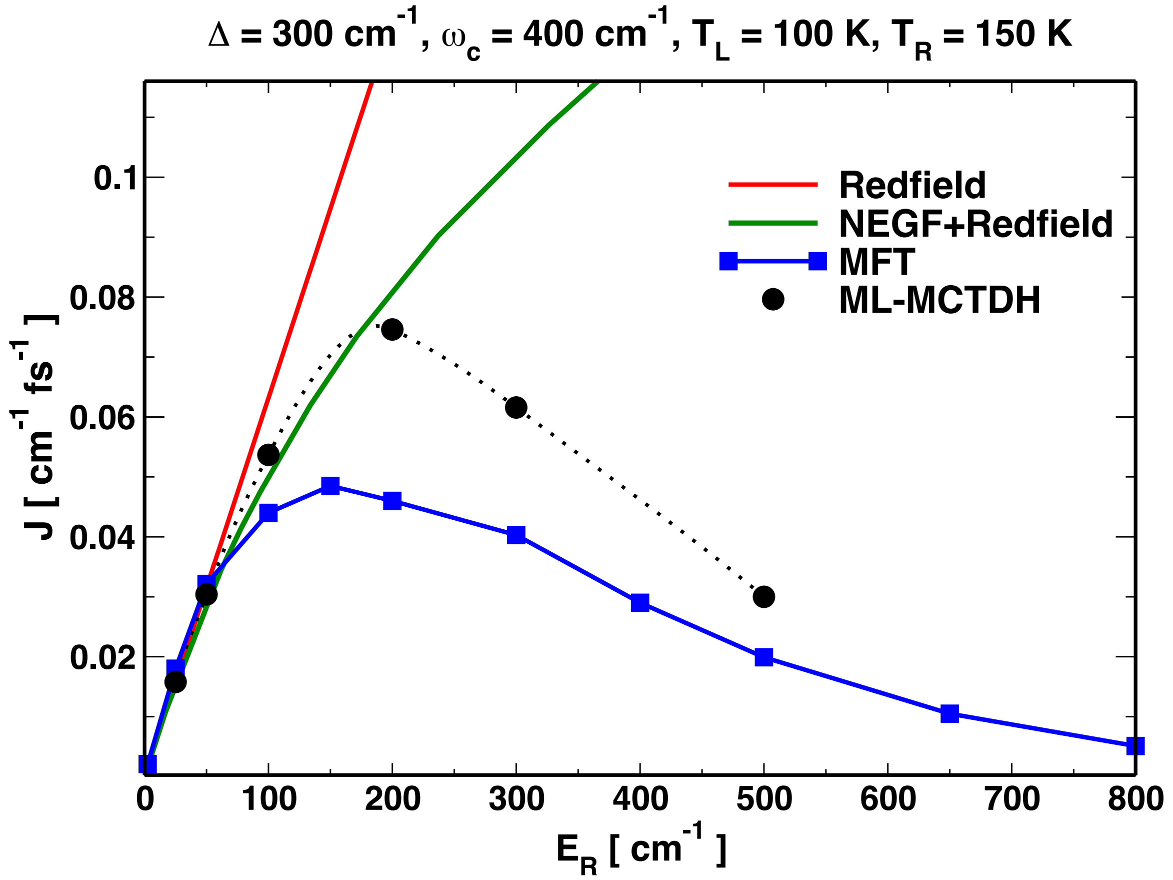
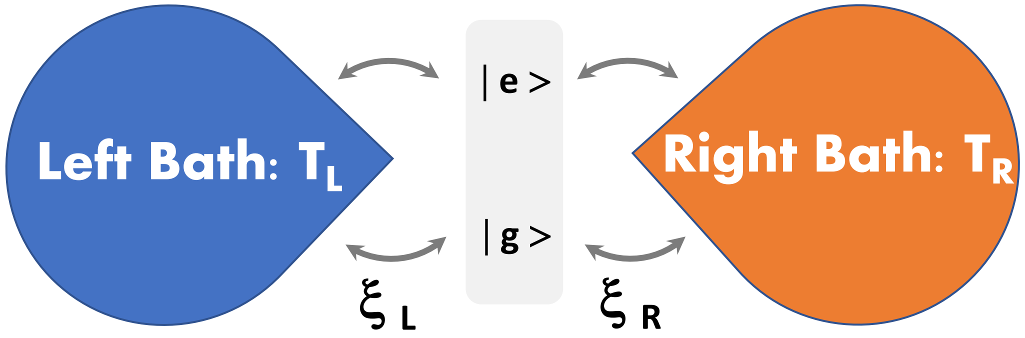
AK, JCP 2019

Heat Transport through a Molecular Junction





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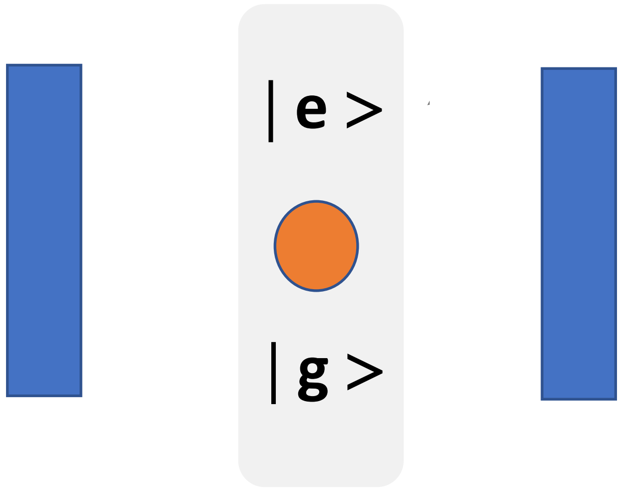
AK, JCP 2019

Spontaneous Emission of Radiation (in a Cavity)



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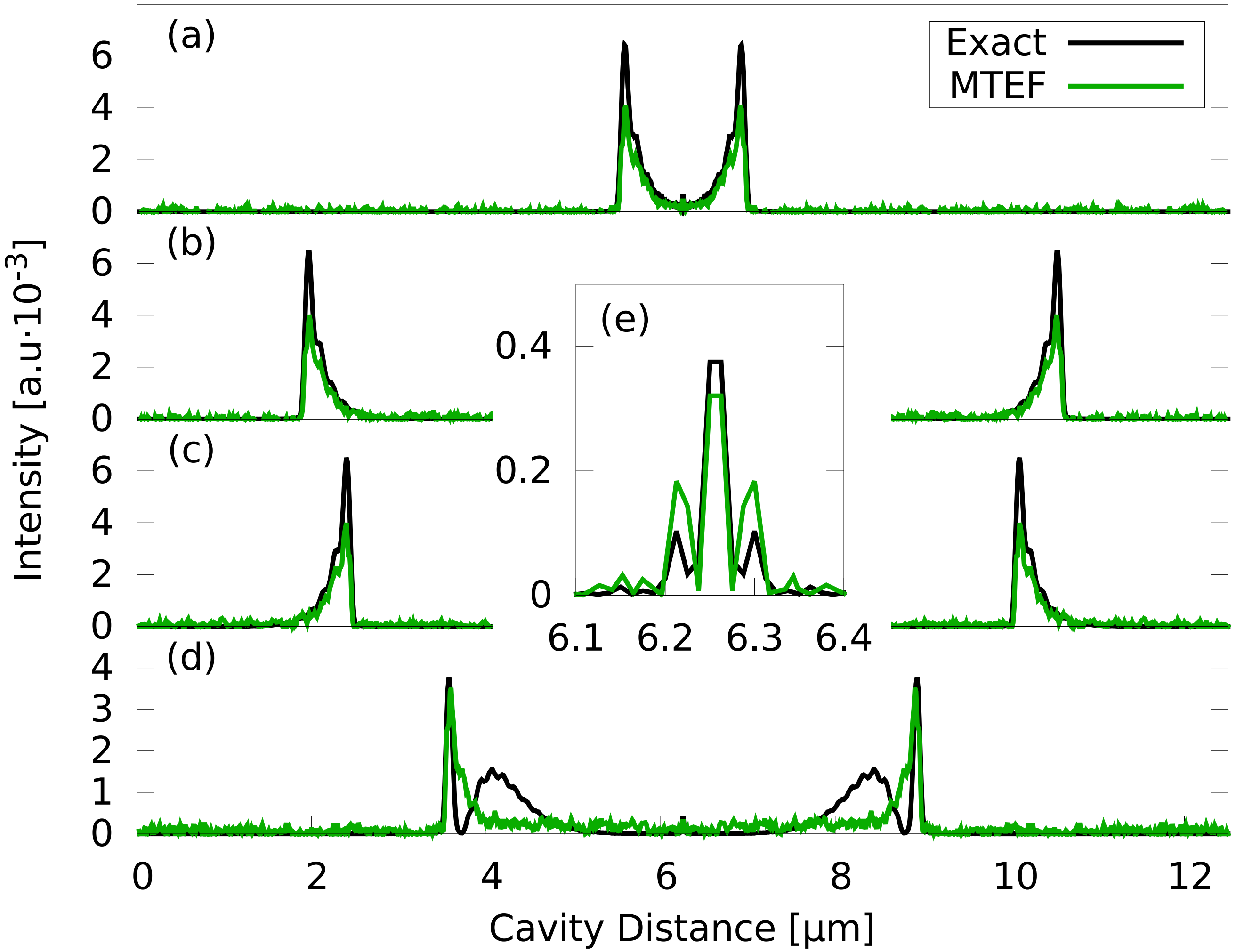
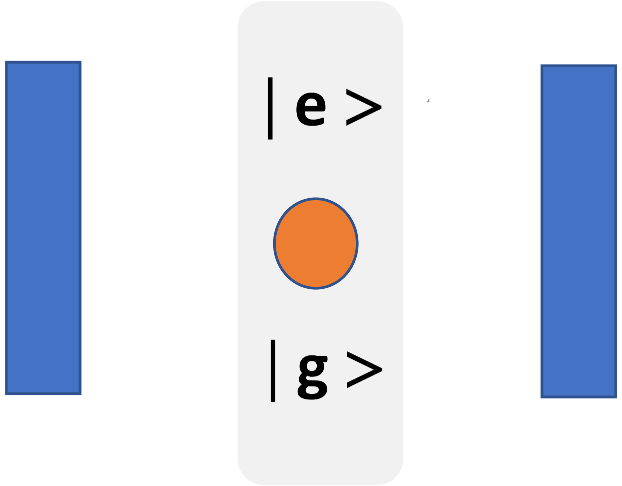
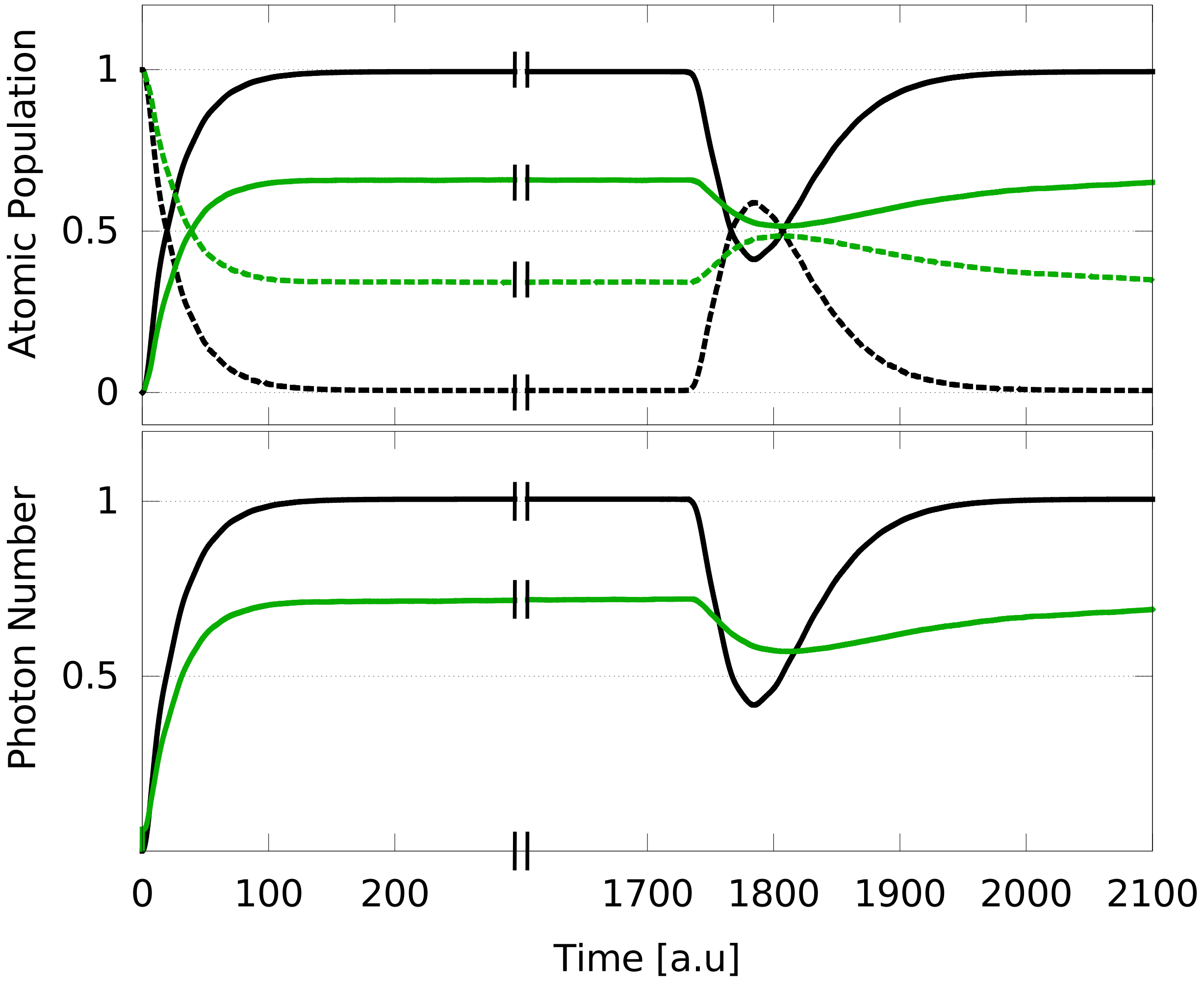
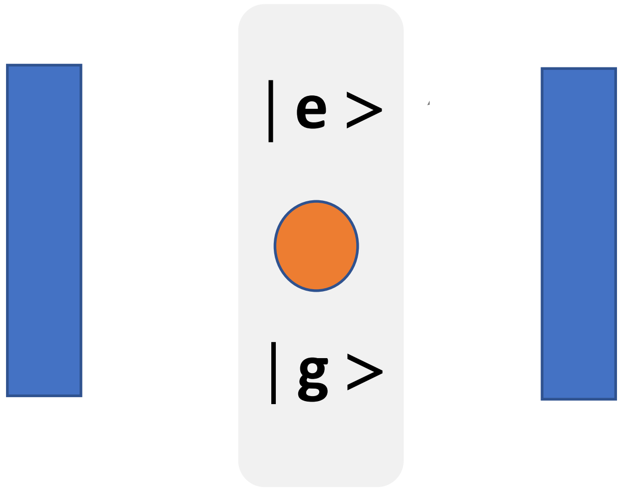




Norah Hoffmann et al., PRA 2019

Spontaneous Emission of Radiation (in a Cavity)





Norah Hoffmann et al., PRA 2019

The Generalized Quantum Master Equation: Reduced Dynamics

Liouville – von Neumann Equation

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]$$

The Generalized Quantum Master Equation: Reduced Dynamics

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)]$$

Projection Operators

Algebra

$$\frac{d}{dt}\hat{\rho}_s(t) = -\frac{i}{\hbar}\mathcal{L}_s\hat{\rho}_s(t) - \int_0^t d\tau\mathcal{K}(\tau)\hat{\rho}_s(t-\tau)$$

Nakajima, Zwanzig, Mori

The Generalized Quantum Master Equation

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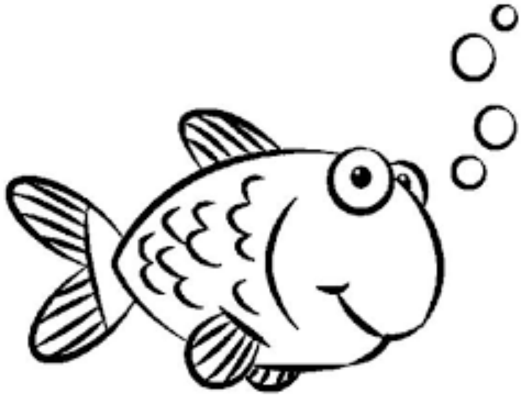
Simple : $\mathcal{L}_s = [\hat{H}_s, \cdot]$

Not so simple : $\mathcal{K}(\tau)$



The Generalized Quantum Master Equation

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Simple : $\mathcal{L}_s = [\hat{H}_s, \cdot]$

Not so simple : $\mathcal{K}(\tau)$

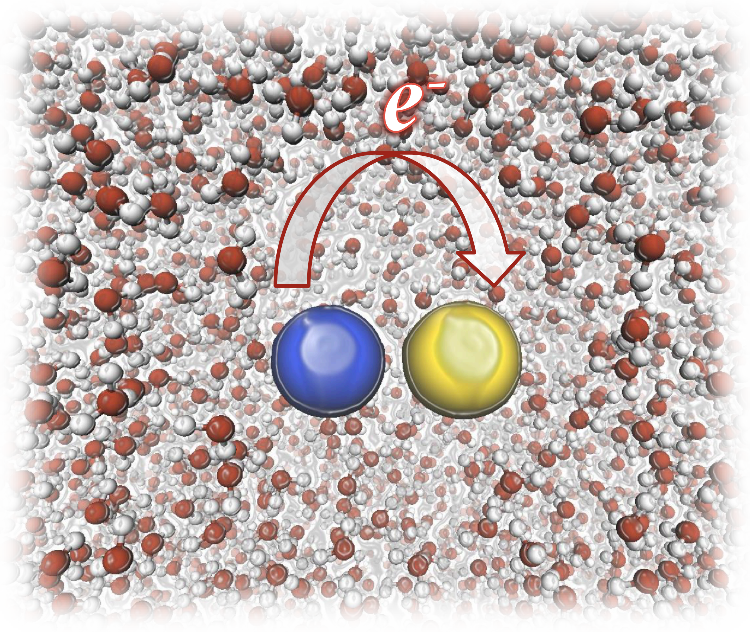
$$\mathcal{K}(t) = \mathcal{K}_1(t) - i\int_0^t d\tau\ \mathcal{K}_3(t-\tau)\mathcal{K}(\tau)$$

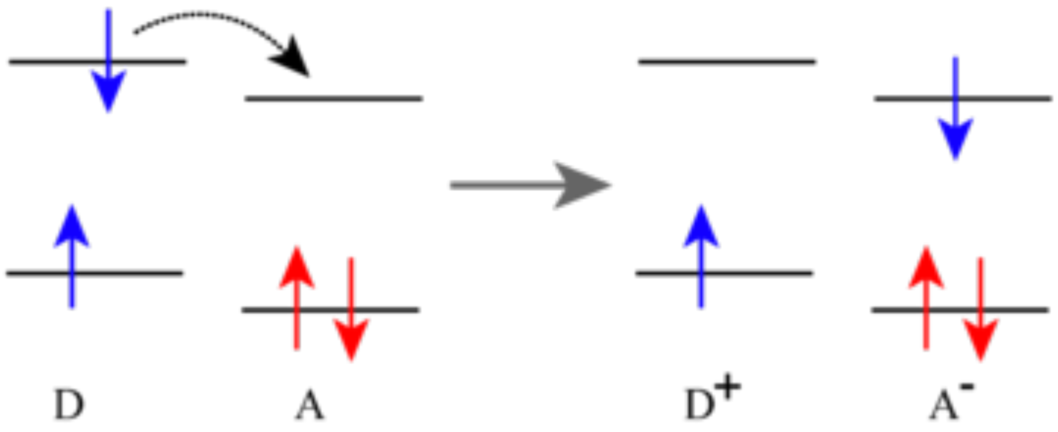
$$\mathcal{K}_1(\tau) = Tr_b\{\mathcal{L}_{sb}e^{-i\mathcal{L}\tau}\mathcal{L}_{sb}\hat{\rho}_b^{eq}\}$$

$$\mathcal{K}_3(\tau) = Tr_b\{e^{-i\mathcal{L}\tau}\mathcal{L}_{sb}\hat{\rho}_b^{eq}\}$$

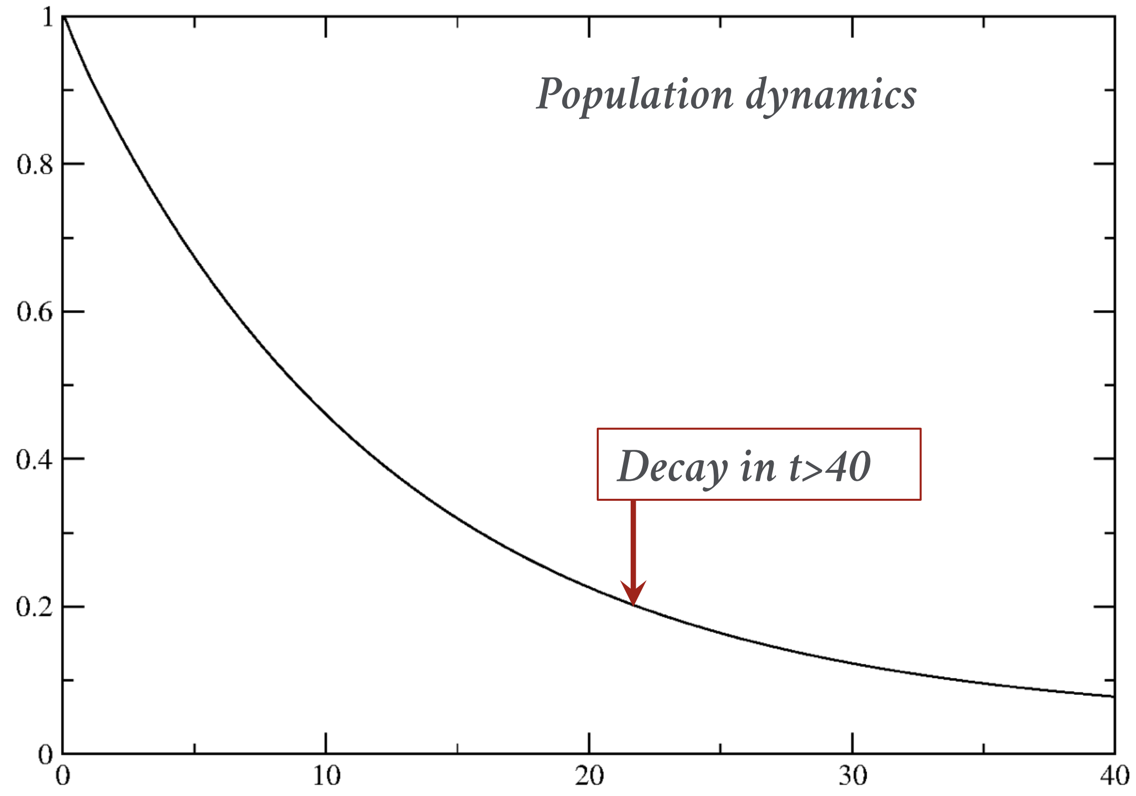
Qiang Shi and Eitan Geva, J. Chem. Phys., 2003

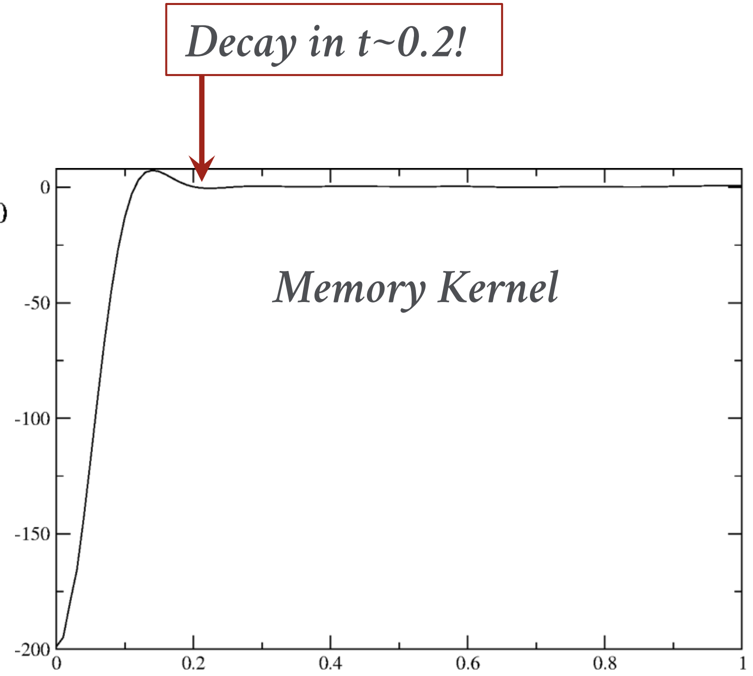
Photo-induced Electron Transfer





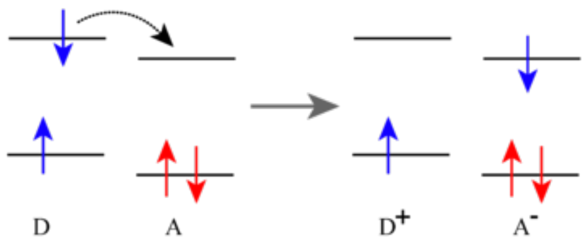
Disparate Time Scales in the Electron – Transfer Regime Lead to Massive Computational Speed-ups

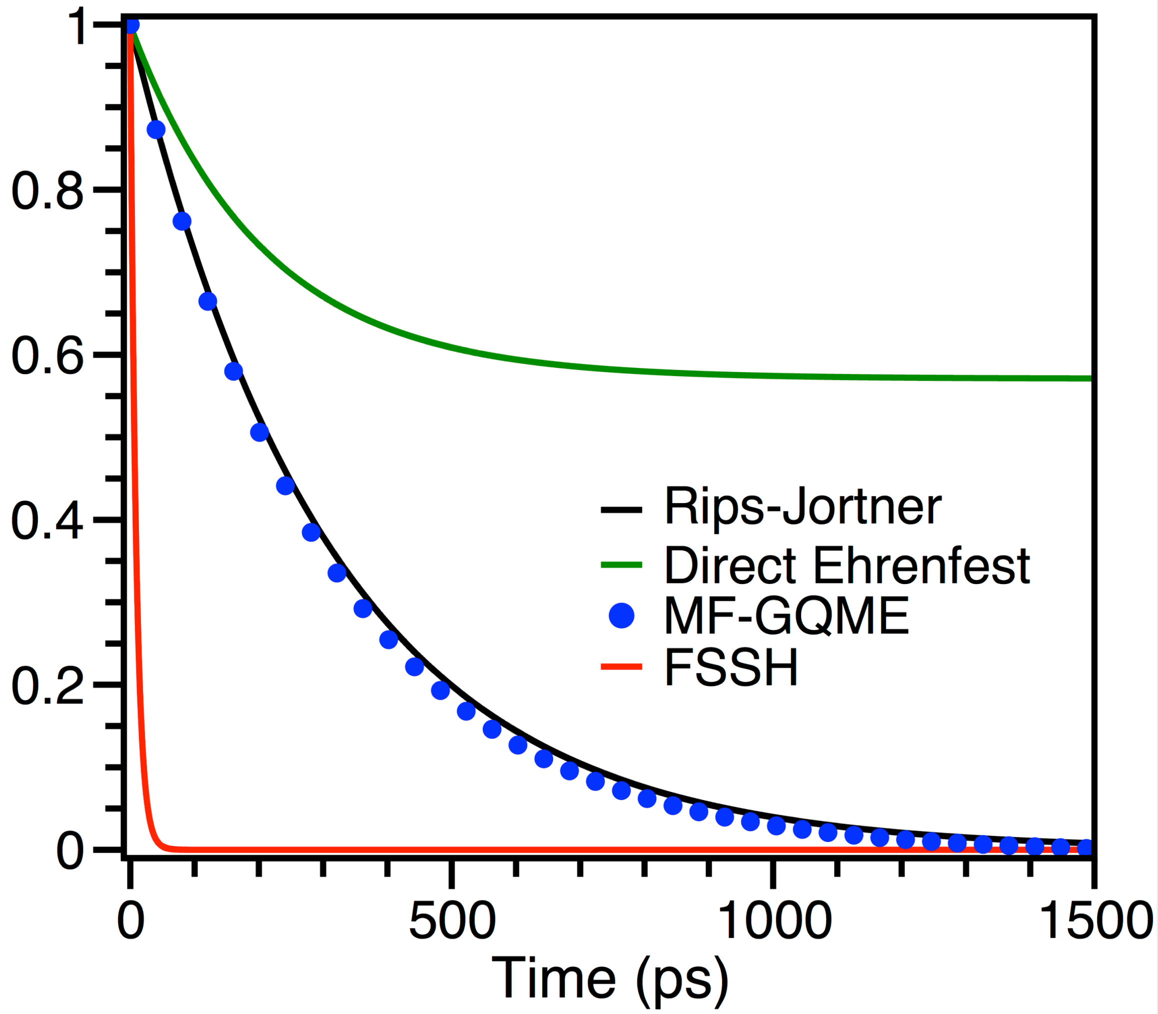




Memory kernel decays ~100 times faster than population.

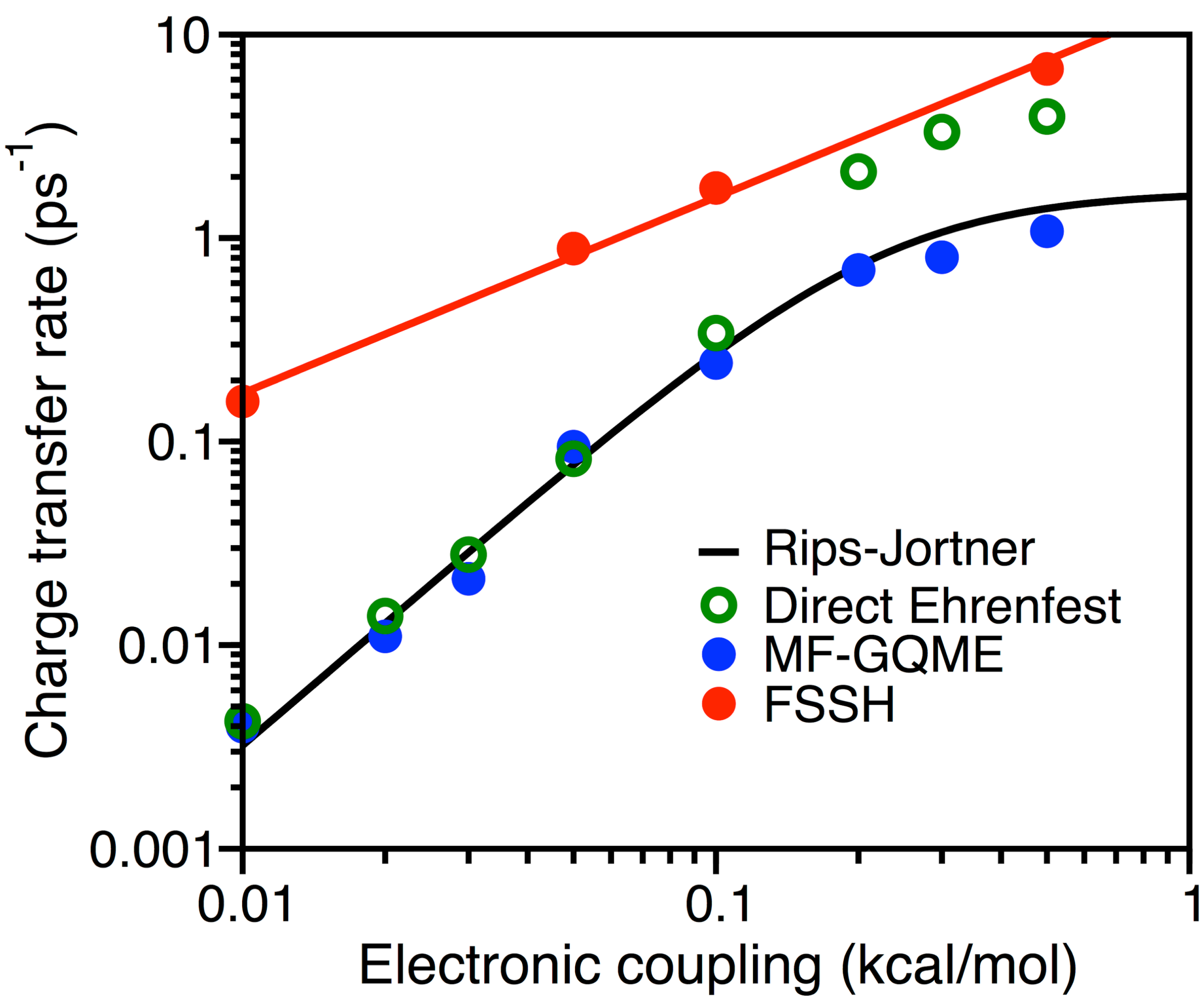
Donor State Population Evolution

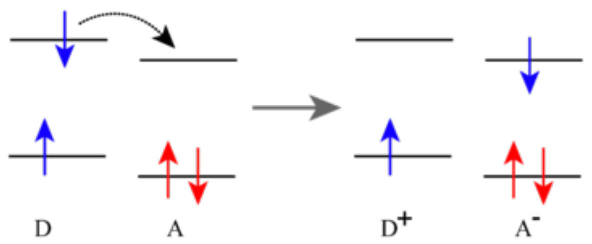




Pfalzgraff, Kelly, and Markland, JPCL, 2015.

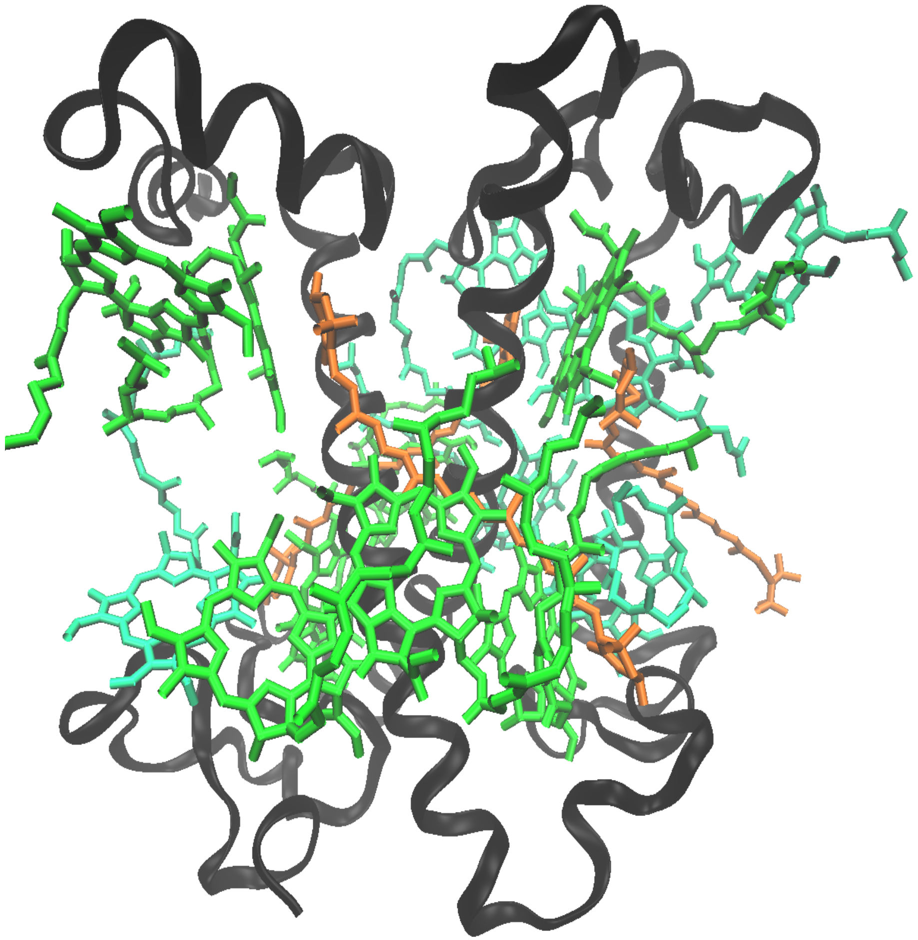
Electron Transfer Rates



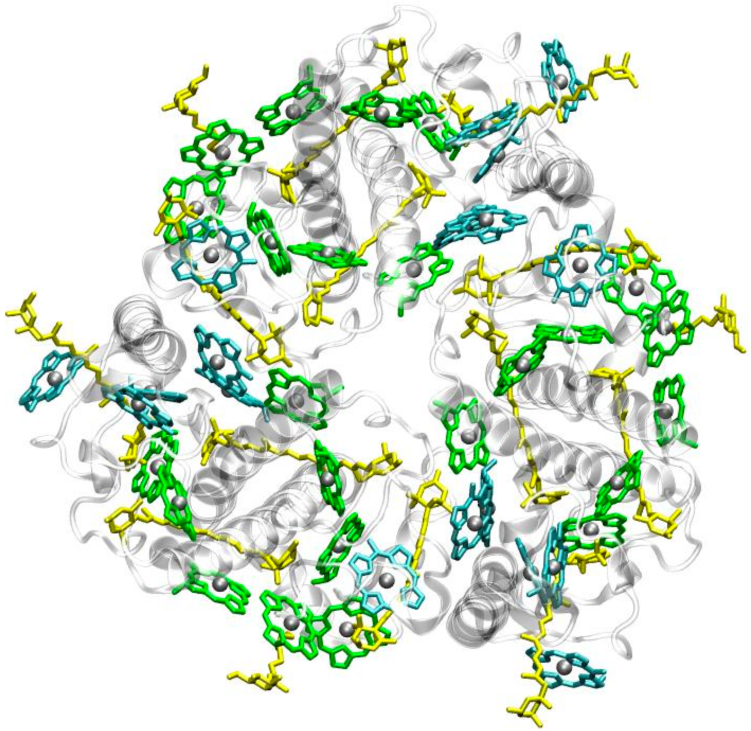


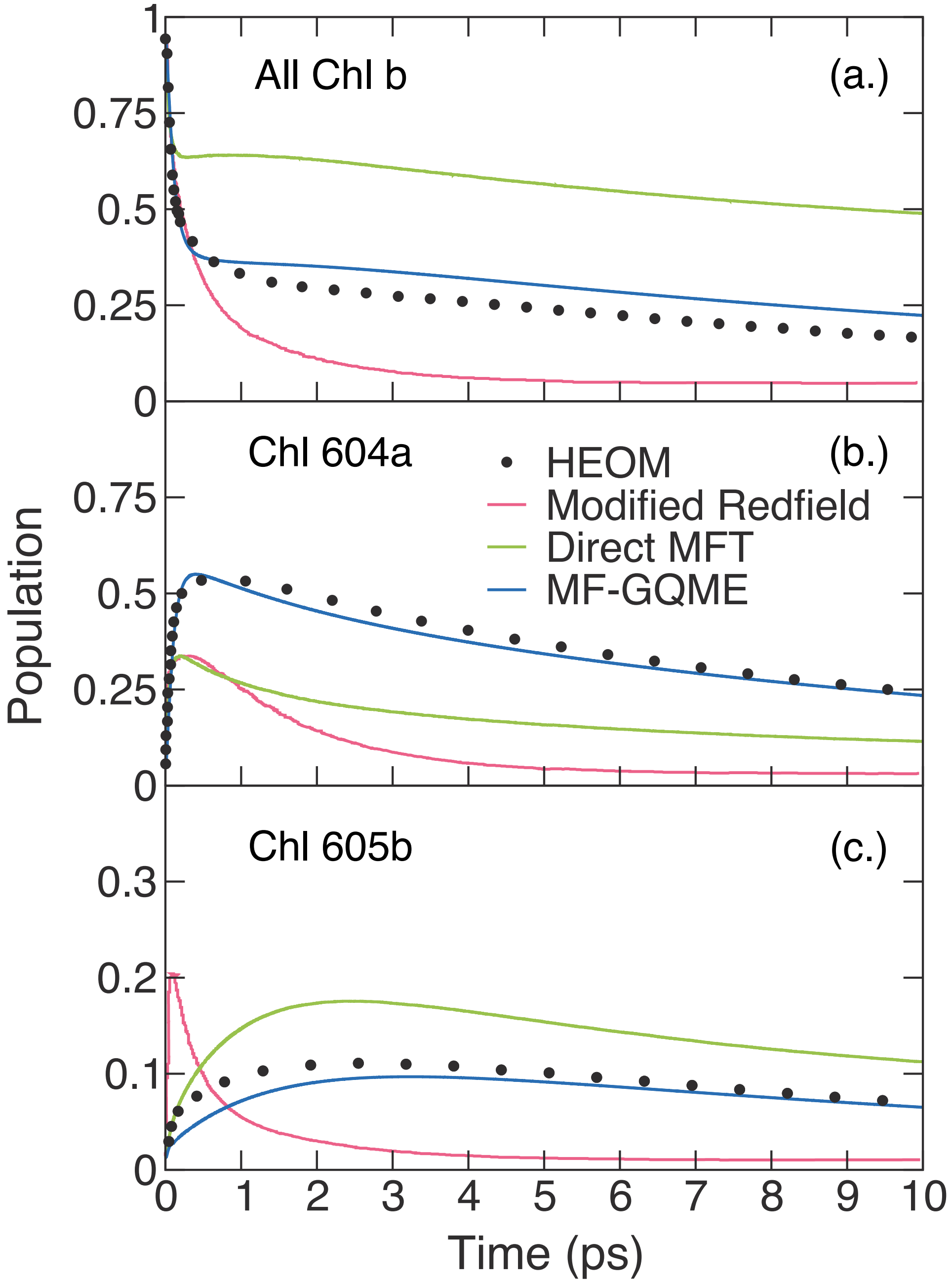
Pfalzgraff, Kelly, and Markland, JPCL, 2015.

Exciton Transport in LHC-II



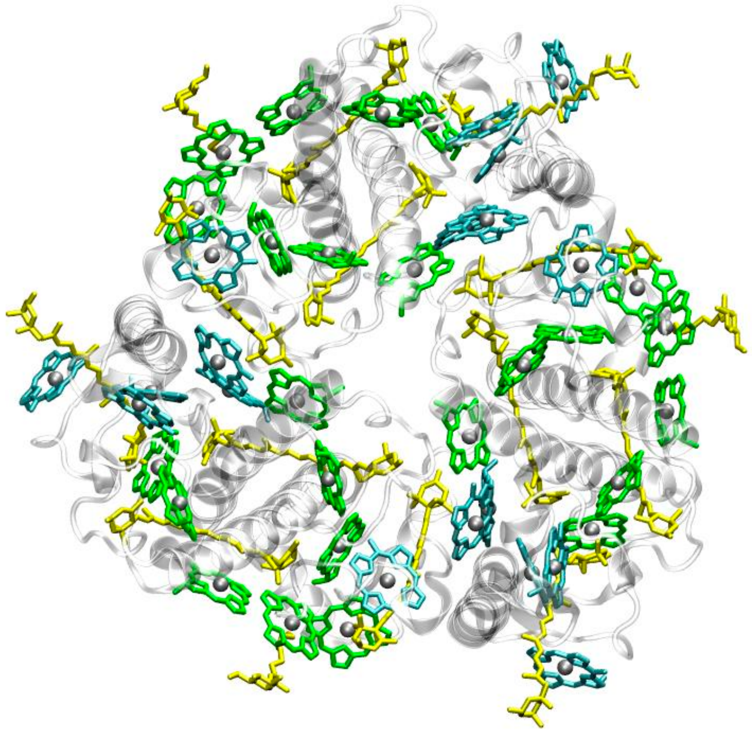
Exciton Transport in LHC-II

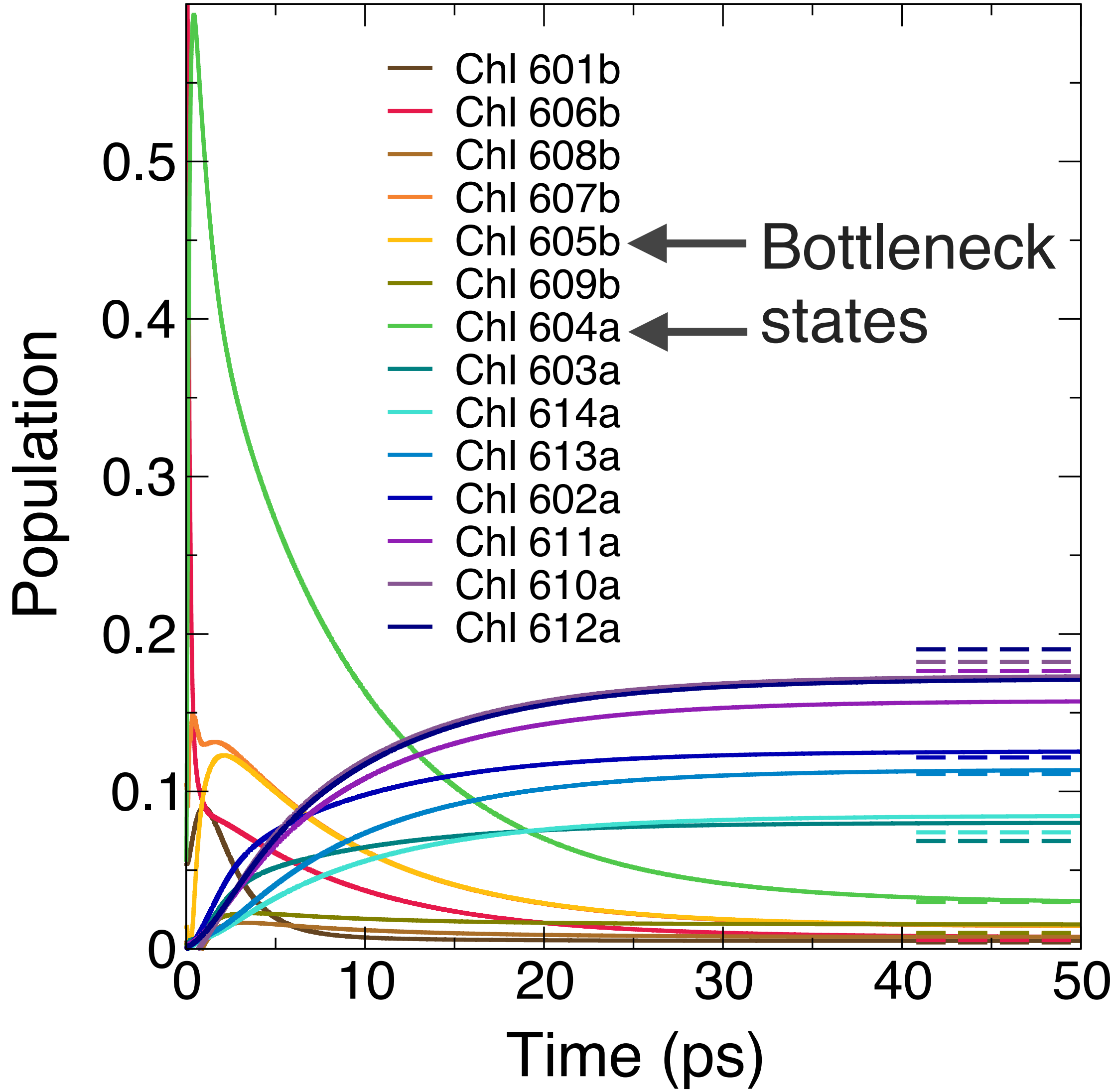




W. Pfalzgraff, A. Montoya-Castillo, A. Kelly, and T.E. Markland, JCP, 2019.

Exciton Transport in LHC-II





W. Pfalzgraff, A. Montoya-Castillo,
A. Kelly, and T.E. Markland, JCP, 2019.

Going Beyond Mean Field Theory: Mapping - QCLE

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar}\overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

Going Beyond Mean Field Theory: Mapping - QCLE

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar}\overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

$$\dot{r}_\lambda = \frac{\partial H_m}{\partial p_\lambda}, \quad \dot{p}_\lambda = -\frac{\partial H_m}{\partial r_\lambda}, \quad \dot{R} = \frac{\partial H_m}{\partial P},$$

$$\dot{P} = -\frac{\partial H_m}{\partial R} + \frac{\hbar}{8\rho_m^{\mathcal{P}}}\frac{\partial \overline{h}^{\lambda\lambda'}}{\partial R}\left(\frac{\partial^2}{\partial r_{\lambda'}\partial r_\lambda} + \frac{\partial^2}{\partial p_{\lambda'}\partial p_\lambda}\right)\rho_m^{\mathcal{P}}$$

Going Beyond Mean Field Theory: Mapping - QCLE

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar}\overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

$$\dot{r}_\lambda = \frac{\partial H_m}{\partial p_\lambda}, \qquad \dot{p}_\lambda = -\frac{\partial H_m}{\partial r_\lambda}, \qquad \dot{R} = \frac{\partial H_m}{\partial P},$$

$$\dot{P} = -\frac{\partial H_m}{\partial R} + \boxed{\frac{\hbar}{8\rho_m^{\mathcal{P}}}\frac{\partial \overline{h}^{\lambda\lambda'}}{\partial R}\left(\frac{\partial^2}{\partial r_{\lambda'}\partial r_\lambda} + \frac{\partial^2}{\partial p_{\lambda'}\partial p_\lambda}\right)\rho_m^{\mathcal{P}}}$$

Going Beyond Mean Field Theory

$$H_m(\mathcal{X}) = \frac{P^2}{2M} + V_0(R) + \frac{1}{2\hbar}\overline{h}^{\lambda\lambda'}(R)(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'})$$

Poisson Bracket Mapping Equation

$$\frac{\partial}{\partial t}\rho_m^{\mathcal{P}}(\mathcal{X}, t) = \left\{H_m, \rho_m^{\mathcal{P}}\right\}_{\mathcal{X}} \equiv -i\mathcal{L}_m^{PB}\rho_m^{\mathcal{P}}(\mathcal{X}, t)$$

Going Beyond Mean Field Theory: PBME

$$\overline{B(t)} = \int d\mathcal{X}\ B_m(\mathcal{X})\rho_m^{\mathcal{P}}(\mathcal{X}, t)$$

$$\hat{\rho}_m^{\mathcal{P}}(X) = |m_\lambda\rangle\langle m_\lambda|\hat{\rho}_m(X)|m_{\lambda'}\rangle\langle m_{\lambda'}|$$

$$\overline{B(t)} = \int d\mathcal{X}\ B_m^{\mathcal{P}}(\mathcal{X})\rho_m^{\mathcal{P}}(\mathcal{X}, t)$$

Improving Linearized Semiclassics with "Minimal Effort"

$$P_{n\leftarrow m}(t) = \mathrm{Tr}\left[\hat{\rho}_\mathrm{b} \left|m\right\rangle\left\langle m\right| \mathrm{e}^{\mathrm{i}\hat{H}t} \left|n\right\rangle\left\langle n\right| \mathrm{e}^{-\mathrm{i}\hat{H}t}\right]$$

$$\left|n\right\rangle\left\langle n\right| = \frac{1}{S}\left(\hat{\mathbb{I}} + \hat{Q}_n\right)$$

$$\hat{Q}_n = (S-1)\left|n\right\rangle\left\langle n\right| - \sum_{m\neq n}^{S} \left|m\right\rangle\left\langle m\right|$$

Improving Linearized Semiclassics with "Minimal Effort"

$$P_{n\leftarrow m}(t) = \mathrm{Tr}\left[\hat{\rho}_{\mathrm{b}}\,|m\rangle\langle m|\,\mathrm{e}^{\mathrm{i}\hat{H}t}\,|n\rangle\langle n|\,\mathrm{e}^{-\mathrm{i}\hat{H}t}\right]$$

$$|n\rangle\langle n| = \frac{1}{S}\left(\hat{\mathbb{I}} + \hat{Q}_n\right)$$

$$\hat{Q}_n = (S-1)\,|n\rangle\langle n| - \sum_{m\neq n}^{S} |m\rangle\langle m|$$

$$P_{n\leftarrow m}(t) = \frac{1}{S^2}\left(S + \mathrm{Tr}\left[\hat{\rho}_{\mathrm{b}}\hat{\mathbb{I}}\mathrm{e}^{\mathrm{i}\hat{H}t}\hat{Q}_n\mathrm{e}^{-\mathrm{i}\hat{H}t}\right] + \mathrm{Tr}\left[\hat{\rho}_{\mathrm{b}}\hat{Q}_m\mathrm{e}^{\mathrm{i}\hat{H}t}\hat{Q}_n\mathrm{e}^{-\mathrm{i}\hat{H}t}\right]\right)$$

Improving Linearized Semiclassics with "Minimal Effort"

$$\hat{Q}_n = (S-1)\,|n\rangle\langle n| - \sum_{m\neq n}^{S} |m\rangle\langle m|$$

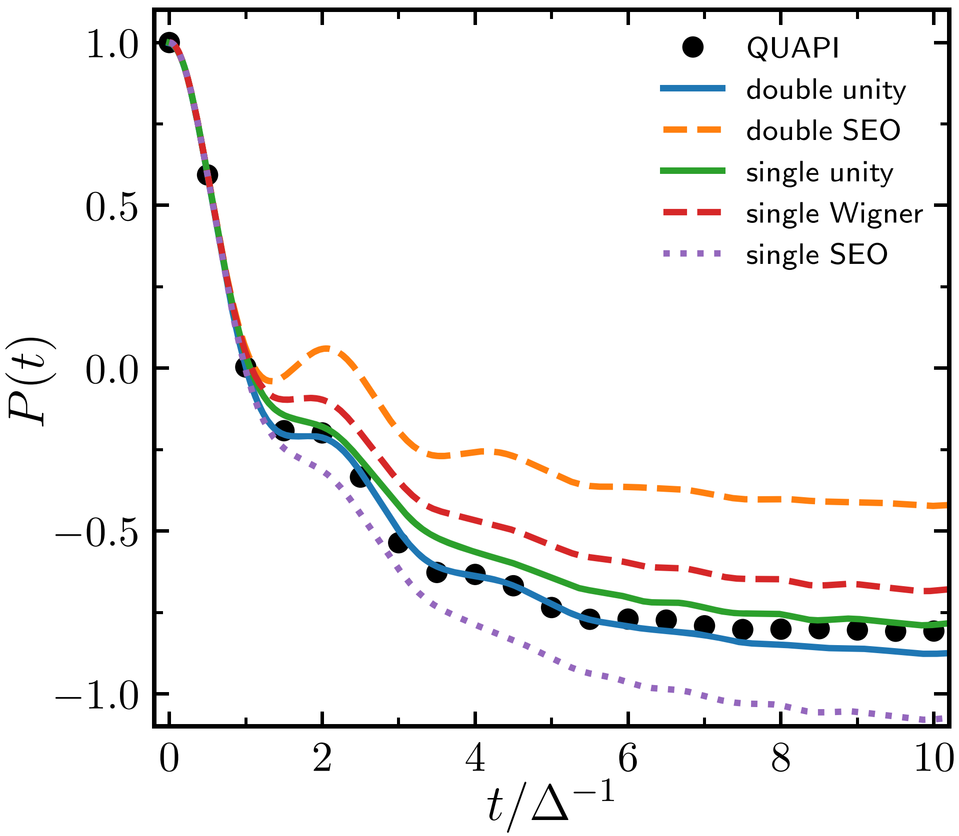
$$P_{n\leftarrow m}(t) = \frac{1}{S^2}\left(S + \mathrm{Tr}\left[\hat{\rho}_\mathrm{b}\hat{\mathbb{I}}\mathrm{e}^{\mathrm{i}\hat{H}t}\hat{Q}_n\mathrm{e}^{-\mathrm{i}\hat{H}t}\right] + \mathrm{Tr}\left[\hat{\rho}_\mathrm{b}\hat{Q}_m\mathrm{e}^{\mathrm{i}\hat{H}t}\hat{Q}_n\mathrm{e}^{-\mathrm{i}\hat{H}t}\right]\right)$$

$$C_{\mathbb{I}Q_n}(t) = \left\langle \phi^a(\mathsf{X},\mathsf{P})\,Q_n(\mathsf{X}(t),\mathsf{P}(t))\right\rangle$$

$$C_{Q_mQ_n}(t) = \langle \phi^a(\mathsf{X},\mathsf{P})\,Q_m(\mathsf{X},\mathsf{P})\,Q_n(\mathsf{X}(t),\mathsf{P}(t))\rangle$$

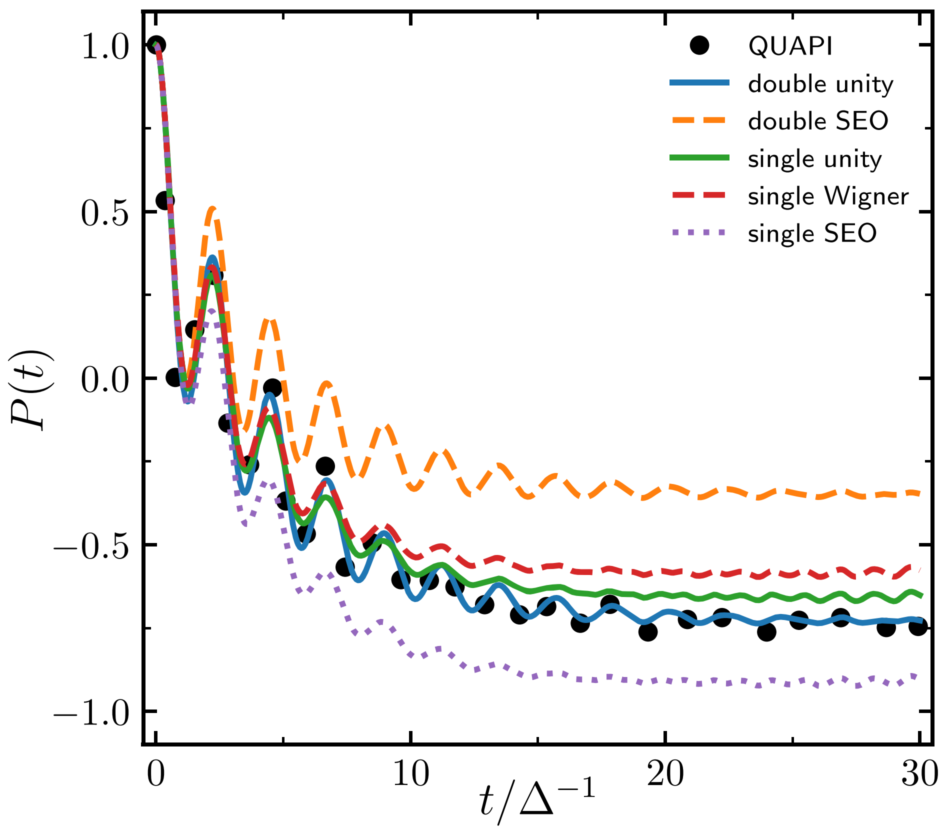
Improving Linearized Semiclassics with "Minimal Effort"

Ohmic Spectral Density



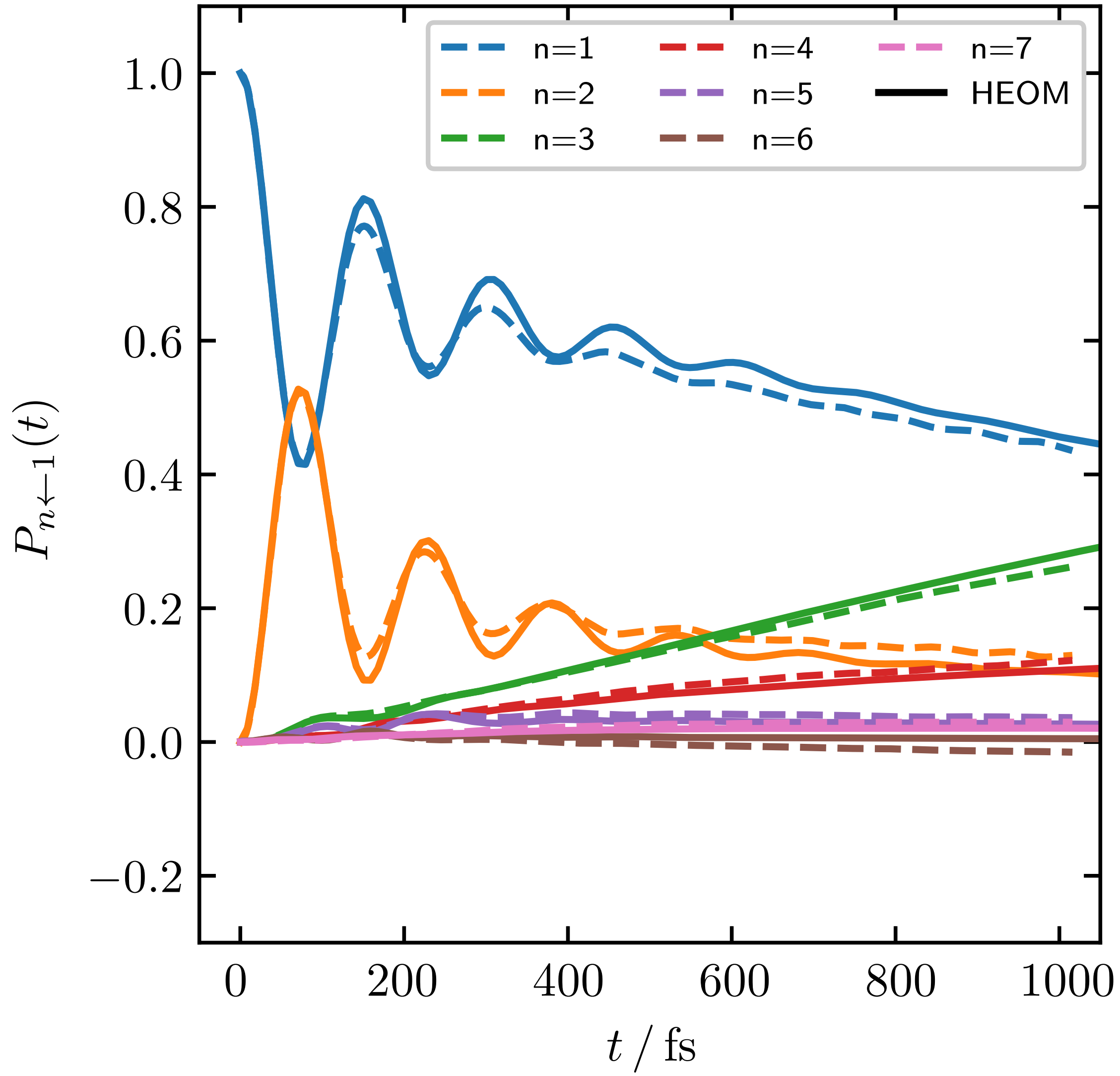
$\varepsilon = \Delta$, $\beta = 5\Delta^{-1}$, $\omega_c = 2\Delta$, and $\xi = 0.4$.

Debye Spectral Density



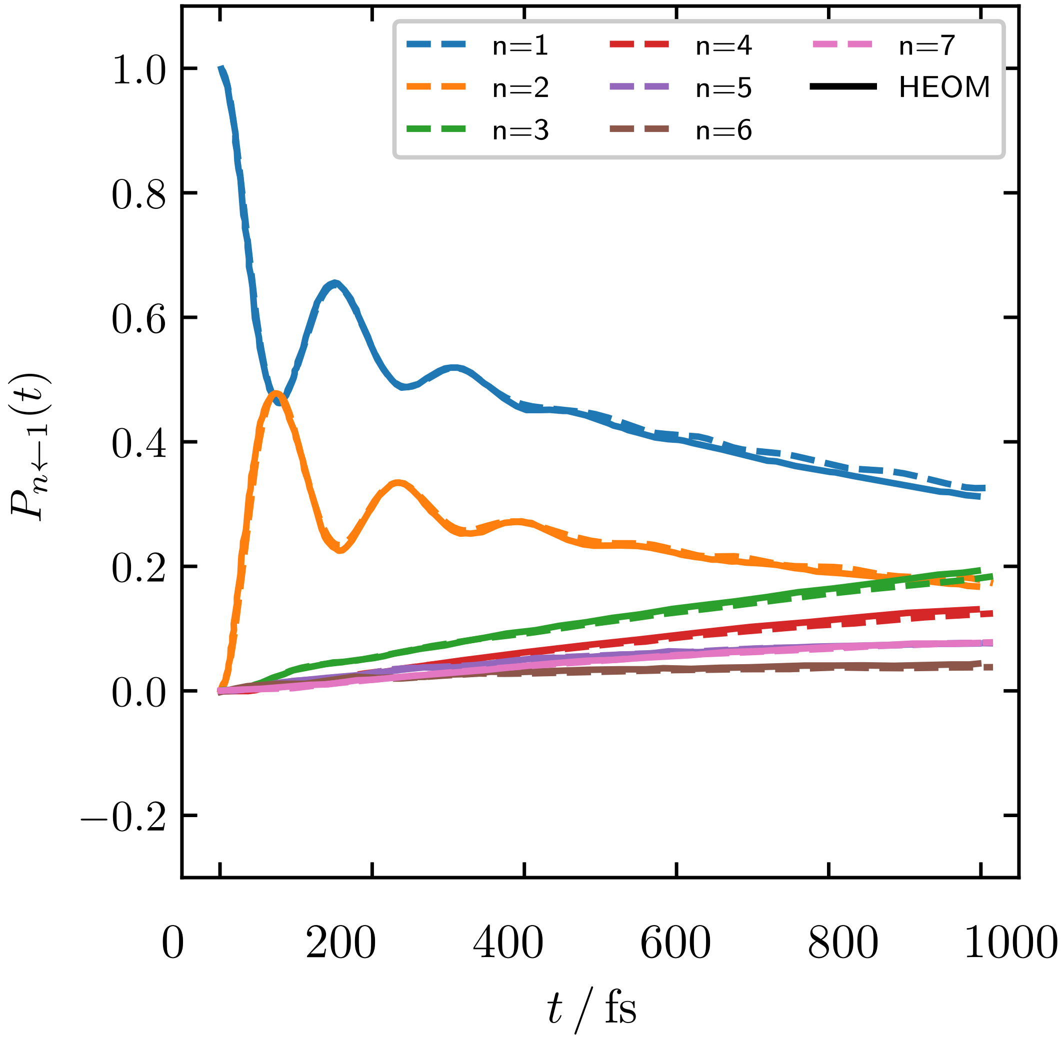
$\varepsilon = \Delta$, $\beta = 50\Delta^{-1}$, $\omega_c = 5\Delta$, and $\eta = 0.5$.

Improving Linearized Semiclassics with "Minimal Effort"



T = 77 K

Improving Linearized Semiclassics with "Minimal Effort"



T = 300 K

Going Beyond Mean Field Theory (II)

Recall: Mean Field Theory

$$\Psi(r, R, t) = \psi(r, t)\chi(R, t)$$

Coupled Mean-Field Trajectories

Recall: Mean Field Theory

$$\Psi(r, R, t) = \psi(r, t)\chi(R, t)$$

Wavefunction Ansatz:

$$|\psi(t,\theta)\rangle = \hat{U}(0,t)|\alpha\rangle \otimes |z\rangle + e^{i\theta}\hat{U}(0,t)|\beta\rangle \otimes |z'\rangle$$

S. A. Sato, A. Kelly, and A. Rubio, Phys. Rev. B, 2018 (In Press)

Going Beyond Mean Field Theory

$$\langle \hat{B}(t) \rangle = \mathrm{Tr}[\hat{B}(t)\hat{\rho}]$$

$$\langle \hat{B}(t) \rangle = \sum_{\alpha\beta} \int \frac{d^2 z}{\pi^{N_b}} \int \frac{d^2 z'}{\pi^{N_b}} \{\langle \alpha | \otimes \langle z |\} \hat{\rho} \{|\beta\rangle \otimes |z'\rangle\} \\ \times \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{-i\theta} \langle \psi(t,\theta) | \hat{B} | \psi(t,\theta) \rangle$$

Going Beyond Mean Field Theory

$$\langle \hat{B}(t) \rangle = \mathrm{Tr}[\hat{B}(t)\hat{\rho}]$$

$$\langle \hat{B}(t) \rangle = \sum_{\alpha\beta} \int \frac{d^2 z}{\pi^{N_b}} \int \frac{d^2 z'}{\pi^{N_b}} \{\langle \alpha | \otimes \langle z | \} \hat{\rho} \{ | \beta \rangle \otimes | z' \rangle \} \\ \times \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{-i\theta} \langle \psi(t,\theta) | \hat{B} | \psi(t,\theta) \rangle$$

$$|\psi(t,\theta)\rangle = \hat{U}(0,t)|\alpha\rangle \otimes |z\rangle + e^{i\theta} \hat{U}(0,t)|\beta\rangle \otimes |z'\rangle$$

Dynamics Algorithm from the Time-Dependent Variational Principle

$$|\tilde{\psi}(t)\rangle = |\alpha(t)\rangle \otimes |z(t)\rangle + |\beta(t)\rangle \otimes |z'(t)\rangle$$

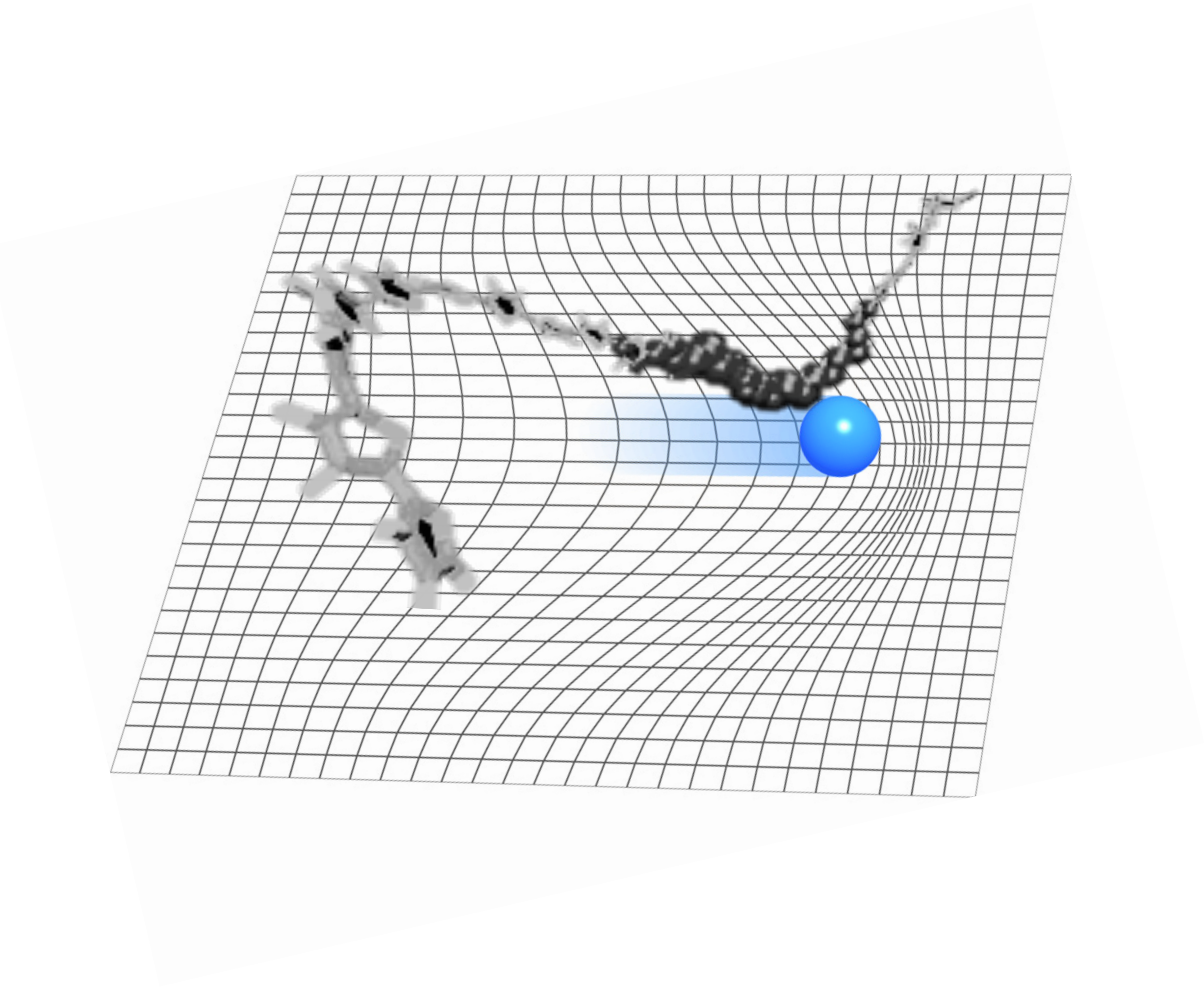
$$L = i\hbar \frac{\langle\tilde{\psi}(t)|\dot{\tilde{\psi}}(t)\rangle - \langle\dot{\tilde{\psi}}(t)|\tilde{\psi}(t)\rangle}{2} - \langle\tilde{\psi}(t)|\hat{H}|\tilde{\psi}(t)\rangle$$

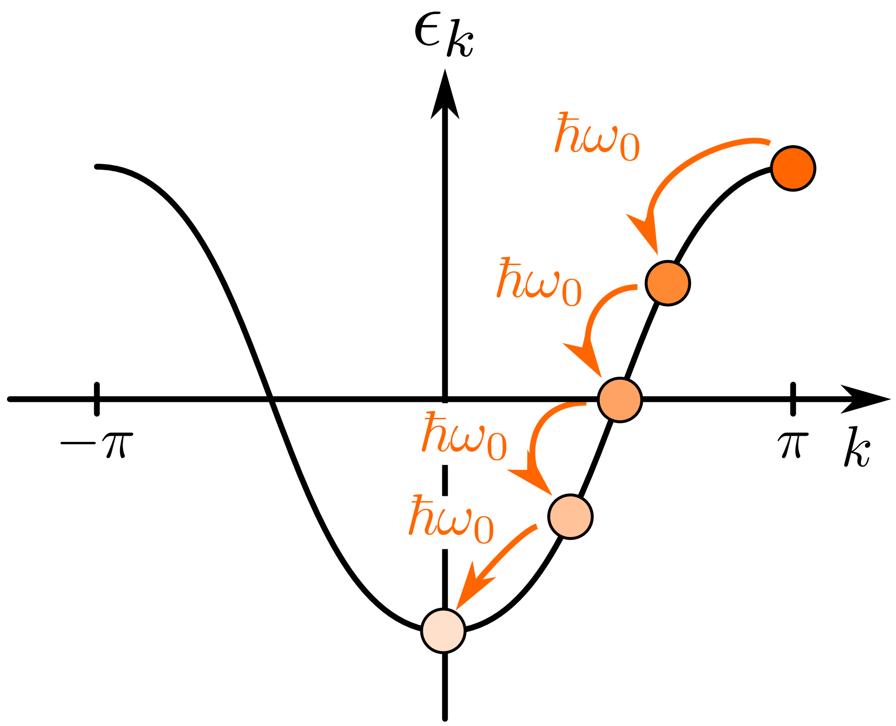
$$\frac{d}{dt}\frac{\partial L}{\partial\langle\dot{\alpha}(t)|} - \frac{\partial L}{\partial\langle\alpha(t)|} = 0$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{z}_n^*} - \frac{\partial L}{\partial z_n^*} = 0$$

S. A. Sato, A. Kelly, and A. Rubio, Phys. Rev. B, 2018.

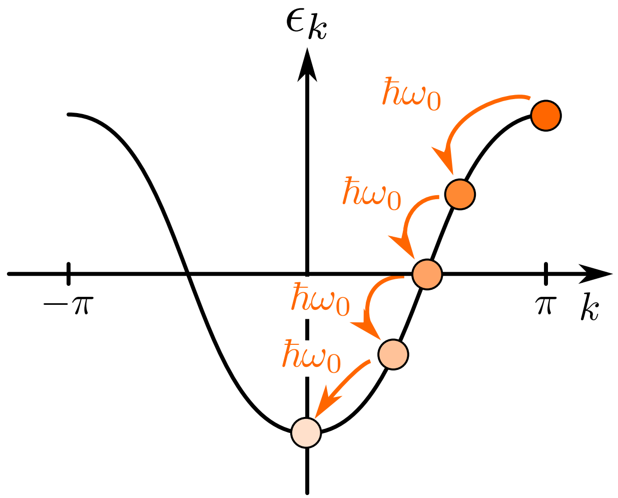
“Molecular Wires” : Charge Transport and Polaron Formation





Holstein Polaron Model

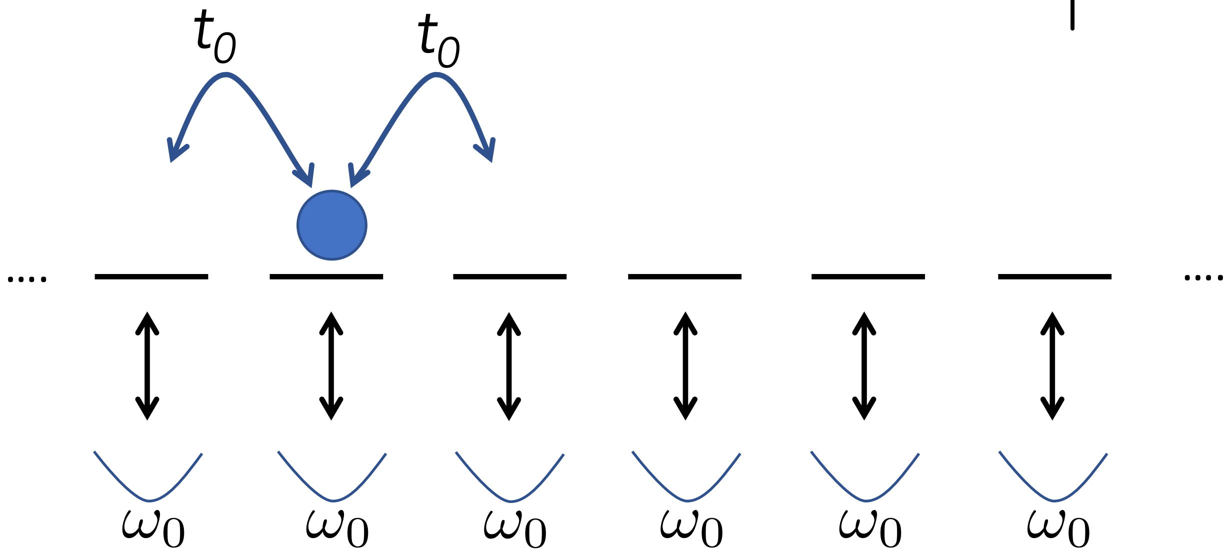
$$\hat{H} = \hat{H}_{kin} + \hat{H}_{ph} + \hat{H}_{coup}$$



$$\hat{H}_{kin} = -t_0 \sum_j \left(c_j^\dagger c_{j+1} + c_{j+1}^\dagger c_j \right)$$

$$\hat{H}_{ph} = \omega_0 \sum_j a_j^\dagger a_j$$

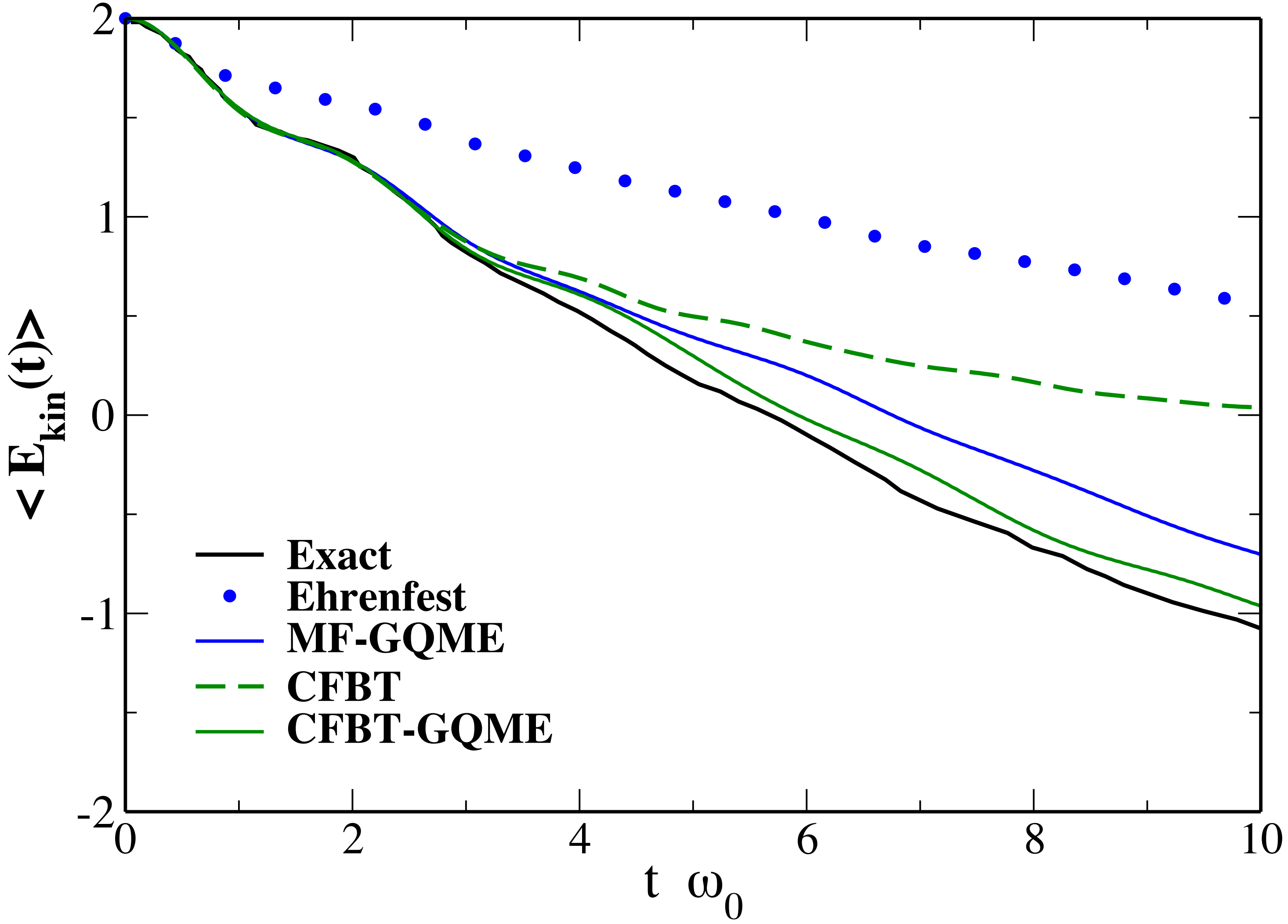
$$\hat{H}_{coup} = -\gamma \sum_j \left(a_j + a^\dagger \right) \hat{n}_j$$

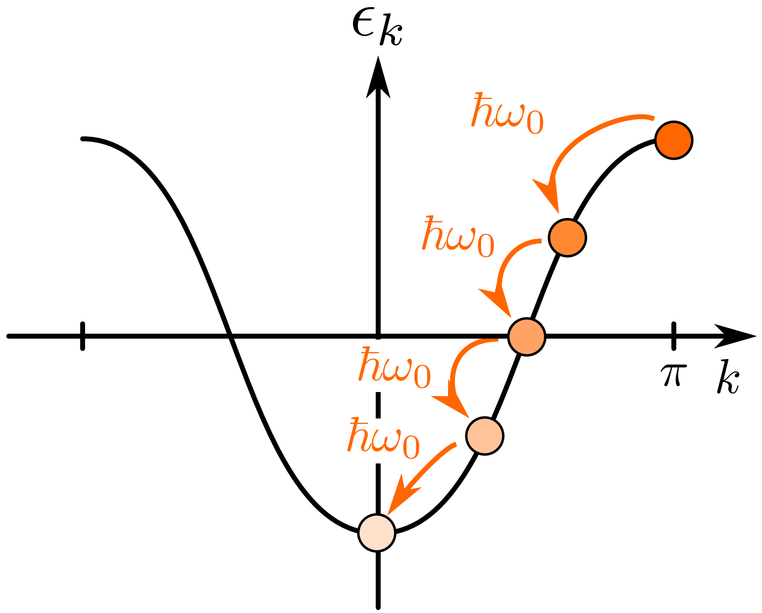


$$\lambda = \frac{\gamma^2}{2 t_0 \omega_0}$$

+ Periodic Boundary Conditions

Real-time Dynamics of Polaron Formation (at zero Kelvin)





S.A. Sato, A. Rubio, and A. Kelly, (In Progress)

Summary

- ***Trajectory-based quantum-classical approaches to quantum dynamics can accurately capture the physics of a wide range of energy and charge transfer problems.***

- ***Applications to spectroscopy and transport properties are ongoing.***

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