Electronically Non-Adiabatic Dynamics via a Symmetrical Quasiclassical Windowing Model

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all with Stephen J. Cotton

Generalization to N electronic States

(HD Meyer & WH Miller, JCP 1979)

\ Consider t-dep Schrödinger equation for N electronic states, with nuclei following trajectory ***R(t)***:

$$i\hbar\ \dot{c}_k(t) = \sum_{k'=1}^{N} H_{k,k'}(t)\ c_{k'}(t) \qquad *$$

$H_{k,k'}(\mathbf{R}(t))$ = diabatic electronic matrix

Let $c_k(t) \equiv \sqrt{n_k(t)}\ e^{-iq_k(t)}$, and define

$$H_{el}(\mathbf{n},\mathbf{q};t) \equiv \sum_{k,k'=1}^{N} c_k^{*} H_{k,k'}(t)\ c_{k'}(t)$$

$$= \sum_{k=1}^{N} n_k H_{kk}(t) + \sum_{k<k'=1}^{N} \sqrt{(n_k+\tfrac{1}{2})(n_{k'}+\tfrac{1}{2})}\ \cos(q_k - q_{k'}) H_{kk'}(t)$$

then Hamilton's (classical) equations of motion

$$\dot{q}_k(t) = \frac{\partial H_{el}}{\partial n_k}\ ,\quad \dot{n}_k(t) = -\frac{\partial H_{el}}{\partial q_k}\ ,$$

are equivalent to the above t-dep Schrödinger Eqn.*

\ Thus the **classical electronic Hamiltonian** for nuclear position **R** is

$$H_{el}(\mathbf{n},\mathbf{q};\mathbf{R}) = \sum_{k=1}^{N} n_k H_{k,k}(\mathbf{R})$$

$$+ \sum_{k<k'=1}^{N} \sqrt{(n_k + \tfrac{1}{2})(n_{k'} + \tfrac{1}{2})}\ \cos(q_k - q_{k'}) H_{kk'}(R)$$

and the total (vibronic) Hamiltonian for electronic and nuclear dof is

$$H(\mathbf{P},\mathbf{R},\mathbf{n},\mathbf{q}) = \frac{\mathbf{P}^2}{2m} + H_{el}(\mathbf{n},\mathbf{q};\mathbf{R})$$

If one proceeds classically, i.e., the usual quasi-classical approach, one runs classical trajectories with the usual initial conditions for the nuclei, and

$n_k(0) = \delta_{k,k_1}$ if k_1 is the initial electronic state

$q_k(0) = 2\pi\cdot$ RN ,

and histograms the final qu. nos. as usual.
A number of applications were carried out in early 1980's [$F^* + H_2 \rightarrow HF + H$, $Br^* + H_2 \rightarrow Br + H_2^{\ddagger}$, $Na + I \rightarrow Na^+ + I^-$, ...]

Useful (esp for SEMIclassical implementations) to change to Cartesian electronic variables:

$$p_k = -\sqrt{2\left(n_k + \tfrac{1}{2}\right)}\ \sin(q_k)$$

$$x_k = \sqrt{2\left(n_k + \tfrac{1}{2}\right)}\ \cos(q_k)$$

$$H(\mathbf{P},\mathbf{R},\mathbf{p},\mathbf{x}) = \frac{\mathbf{P}^2}{2m} + \sum_{k=1}^{N} \frac{1}{2}(p_k^2 + x_k^2 - 1)\ H_{kk}(\mathbf{R}) + \sum_{k<k'=1}^{N} (p_k p_{k'} + x_k x_{k'})\ H_{kk'}(\mathbf{R})$$

- **NOTE:**
- Stock and Thoss (1997) gave a derivation of this 'classical' vibronic Hamiltonian which shows that it is in fact **not an approximation**, but **rather a representation** of the vibronic system. I.e., if one were to treat this **Hamiltonian fully QM'ly**, one would obtain the **exact** QM vibronic dynamics.

*

More Rigorous Derivation

$$\hat{H} = \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i,j} H_{ij}(\hat{\mathbf{R}})\ \hat{a}_i^\dagger \hat{a}_j$$

Where $\hat{a}_i^\dagger,\ \hat{a}_i$ are the creation and annihilation operators for populating electronic state *i*.

Choosing harmonic oscillators for the underlying DOF, one can express the creation/annihilation operators in terms of Cartesian variables:

$$\hat{a}_i = \frac{\hat{x}_i + i\hat{p}_i}{\sqrt{2}} \quad \hat{a}_i^\dagger = \frac{\hat{x}_i - i\hat{p}_i}{\sqrt{2}} \quad (m = \omega = \hbar = 1)$$

Then:

$$\hat{H} = \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i,j} H_{ij}(\hat{\mathbf{R}})\ \tfrac{1}{2}\left(\hat{p}_i\hat{p}_j + \hat{x}_i\hat{x}_j - \delta_{ij}\right)$$

$$= \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i} H_{ii}(\hat{\mathbf{R}})\ \tfrac{1}{2}\left(\hat{p}_i^2 + \hat{x}_i^2 - 1\right)$$

$$+ \sum_{i<j} H_{ij}(\hat{\mathbf{R}})\ \left(\hat{p}_i\hat{p}_j + \hat{x}_i\hat{x}_j\right)$$

NOTE: Even though the nuclei see the ‘Ehrenfest force; —

$$m\ddot{\mathbf{R}}(t) = -\sum_{k,k'=1}^{N} c_k(t)^* \frac{\partial H_{k,k'}(\mathbf{R})}{\partial \mathbf{R}} c_{k'}(t)$$

—— different electronic transitions have different nuclear trajectories [unlike the Ehrenfest/mean field approximation]

Symmetrical Windowing for Quasi-Classical Trajectory Simulations—a Way to Obtain Approximate Quantum State Information

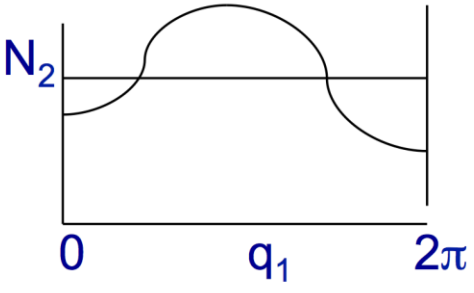
[E.g. vibrational excitation $A + BC(N_1) \rightarrow AB(N_2) + C$ using action-angle variables (n, q) for the vibration DOF]

1. "Exact" Classical Transition Probability

$$P^{QC}_{N_2 \leftarrow N_1} = \frac{1}{2\pi \left| \frac{\partial n_2}{\partial q_1} \right|}$$

where

$$N_1 = n_1$$
$$N_2 = n_2(N_1, q_1)$$



2. Traditional Quasi-Classical (QC) Model

$$P^{QC}_{N_2 \leftarrow N_1} = \frac{1}{2\gamma} \int_{N_2-\gamma}^{N_2+\gamma} dn_2 \, \frac{1}{2\pi \left| \frac{\partial n_2}{\partial q_1} \right|}$$

$$= \frac{1}{2\pi} \int_0^{2\pi} dq_1 \, \frac{1}{2\gamma} \, h\left(\gamma - |n_2(q_1) - N_2|\right)$$

i.e. $n_2 \in [N_2 \pm \gamma]$ ($\gamma = \frac{1}{2}$ in original QC)

3. Symmetrical Quasi-Classical (SQC) Model

Also average over $n_1 \in [N_1 \pm \gamma]$:

$$P^{SQC}_{N_2 \leftarrow N_1} = \frac{1}{2\pi} \int dn_1 \, dq_1 \; W_{N_1}(n_1) \cdot W_{N_2}(n_2)$$

where

$$W_N(n) = \frac{1}{2\gamma} h(\gamma - |n - N|)$$

which is in the form of a phase-space average which one evaluates by Monte Carlo. I.e.:

$$P^{SQC}_{N_2 \leftarrow N_1} = \left\langle W_{N_2}(n_2) \right\rangle$$

using W_{N_1} to sample n_1 and choosing $q_1 \in [0, 2\pi]$

Cf. Quantum Transition Probability

$$
\begin{aligned}
P_{N_2 \leftarrow N_1}(t) &= \left| \langle \psi_{N_2} |\, e^{-i\hat{H}t/\hbar}\, | \psi_{N_1} \rangle \right|^2 \\
&= \langle \psi_{N_1} |\, e^{i\hat{H}t/\hbar}\, | \psi_{N_2} \rangle \, \langle \psi_{N_2} |\, e^{-i\hat{H}t/\hbar}\, | \psi_{N_1} \rangle \\
&= \mathrm{tr} \left[\hat{P}_{N_1} \hat{P}_{N_2}(t) \right]
\end{aligned}
$$

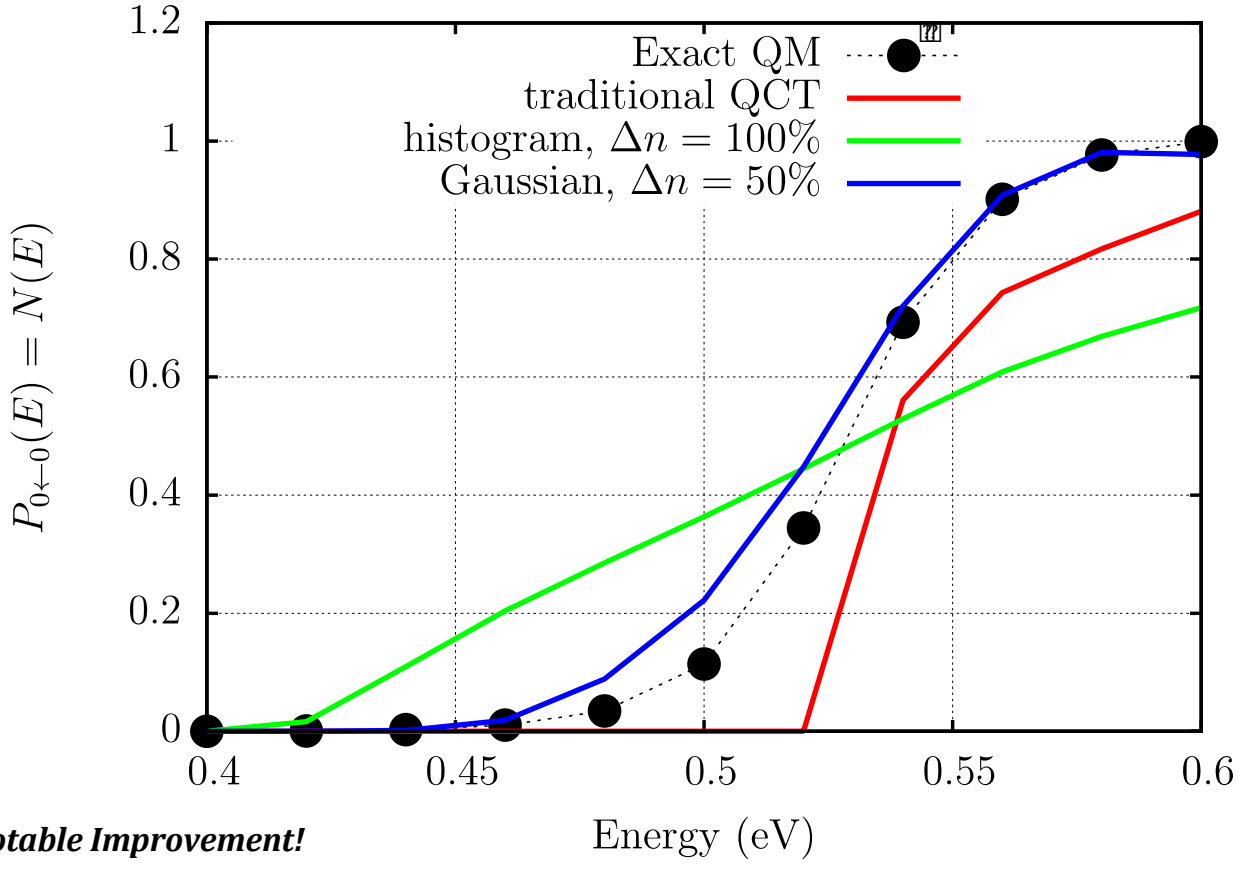
where $\hat{P}_N = |\psi_N\rangle \langle \psi_N|$

$$\hat{P}_N(t) = e^{i\hat{H}t/\hbar}\, \hat{P}_N\, e^{-i\hat{H}t/\hbar}$$

I.e., $\hat{P}_N^{(\mathrm{QM})} \to W_N^{(\mathrm{CI})}(n)$

Summary of $P_{0\leftarrow 0}(E) = N(E)$ Results for H + H_2 over the Threshold Energy Region

SQC using Gaussians:

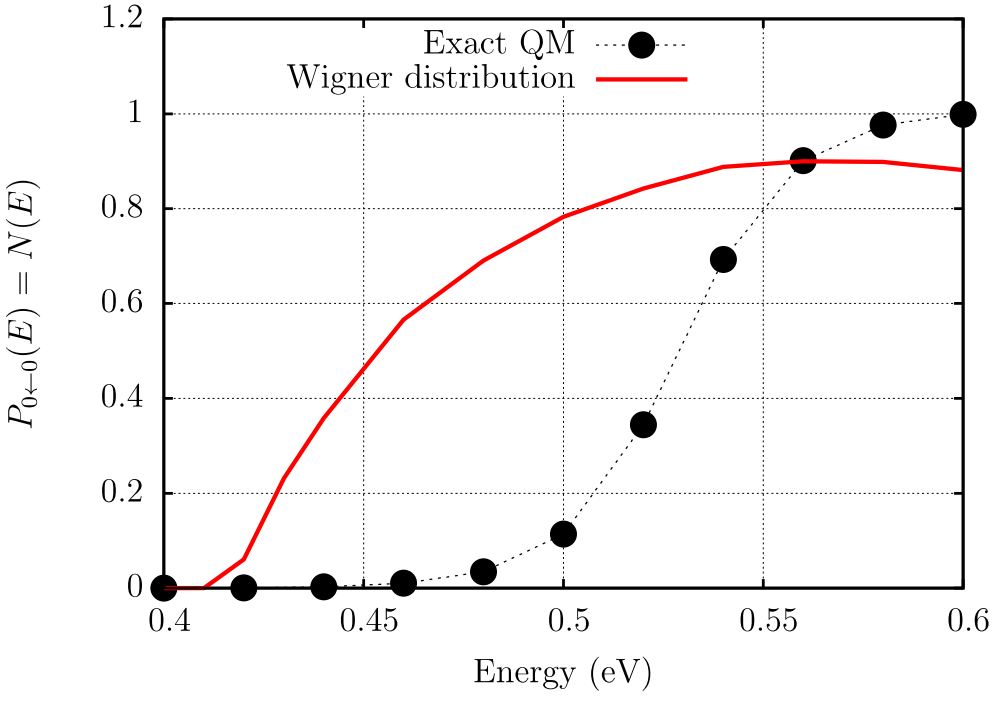


Notable Improvement!

What about the Wigner distribution function?

$W_0^{\mathrm{w}}(n) = 2\mathrm{e}^{-2\left(n+\frac{1}{2}\right)}$

Not so good…



One Justification for the Choice of the γ-Parameter

Any 2-state QM system is isomorphic to a spin-$\frac{1}{2}$ system (having Q-numbers for the z-component of S of $m \pm \frac{1}{2}$) for which, if γ is the maximum deviation from the Q-numbers, the total spin S satisfies:

$$\langle S^2 \rangle = \left(\gamma + \tfrac{1}{2}\right)^2,$$

and therefore

$$\gamma = \sqrt{\langle S^2 \rangle} - \tfrac{1}{2}.$$

Now one can envision 3 possible choices for S^2:

$$\begin{aligned}
\langle S^2 \rangle_{\mathrm{Cl}} &= \left(\tfrac{1}{2}\right)^2 && \Longrightarrow && \gamma = 0 \\
\langle S^2 \rangle_{\mathrm{Langer}} &= \left(\tfrac{1}{2} + \tfrac{1}{2}\right)^2 && \Longrightarrow && \gamma = \tfrac{1}{2} \\
\langle S^2 \rangle_{\mathrm{QM}} &= \tfrac{1}{2} \cdot \left(\tfrac{1}{2} + 1\right) && \Longrightarrow && \gamma = \tfrac{\sqrt{3}-1}{2} \approx 0.366
\end{aligned}$$

SQC Approach Applied to Non-Adiabatic Processes via the Meyer-Miller Classical Electronic Hamiltonian

Summary of the Theory

Nuclear dynamics on multiple (F) electronic potential energy surfaces (PESs) is represented in the Meyer-Miller model via the following classical Hamiltonian:

$$H(\boldsymbol{P},\boldsymbol{R},\boldsymbol{n},\boldsymbol{q}) = \frac{\boldsymbol{P}^2}{2\mu} + \sum_{k=1}^{F} n_k\, H_{kk}(\boldsymbol{R}) + 2\sum_{k<k'=1}^{F} \sqrt{(n_k+\gamma)(n_{k'}+\gamma)}\cos(q_k - q_{k'})\, H_{kk'}(\boldsymbol{R})$$

where:

($\boldsymbol{P}$, $\boldsymbol{R}$) are the nuclear momenta and coordinates;

$\{n_k, q_k\}$ are pairs of classical action-angle variables representing the occupation of electronic state k;

$\{H_{kk'}(\boldsymbol{R})\}$ is an $F\times F$ matrix of diabatic PESs depending parametrically on the nuclear coordinates $\boldsymbol{R}$ (e.g., obtained from an electronic structure calculation); and

γ is a variable parameter which represents the fractional quanta of zero point energy (ZPE) in the model.

Key Point: Tying γ to the width Δn of the window functions—i.e., $\gamma = \frac{1}{2}\Delta n$—addresses the problem of ZPE leakage inherent

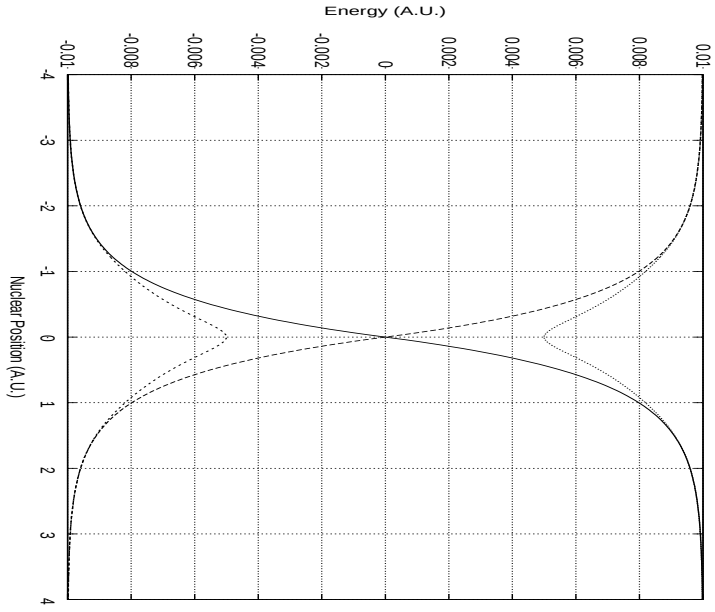
Simple Non-Adiabatic Test Models

Single Avoided Crossing

$$H_{11}(R) = \begin{cases} A(1-e^{-BR}) & R > 0 \\ -A(1-e^{BR}) & R < 0 \end{cases}$$

$$H_{22}(R) = -H_{11}(R)$$

$$H_{12}(R) = H_{21}(R) = Ce^{-DR^2}$$

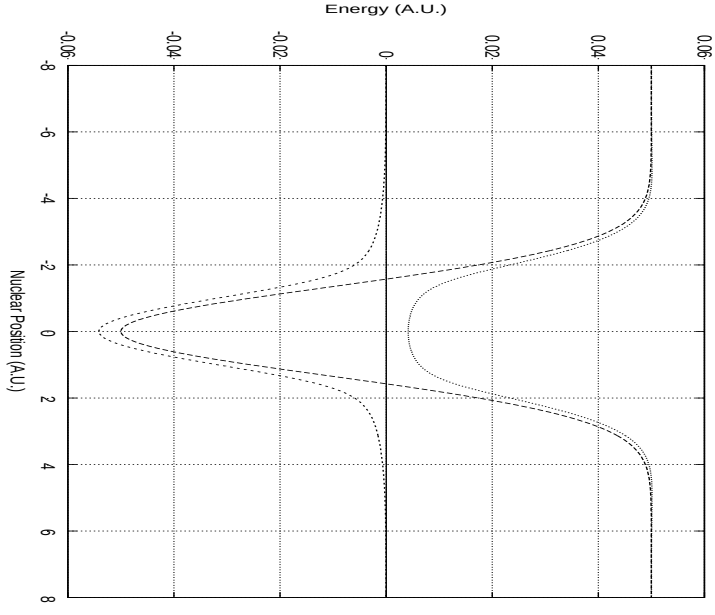


Dual Avoided Crossing

$$H_{11}(R) = 0$$

$$H_{22}(R) = -Ae^{-Bx^2} + E_0$$

$$H_{12}(R) = H_{21}(R) = Ce^{-DR^2}$$



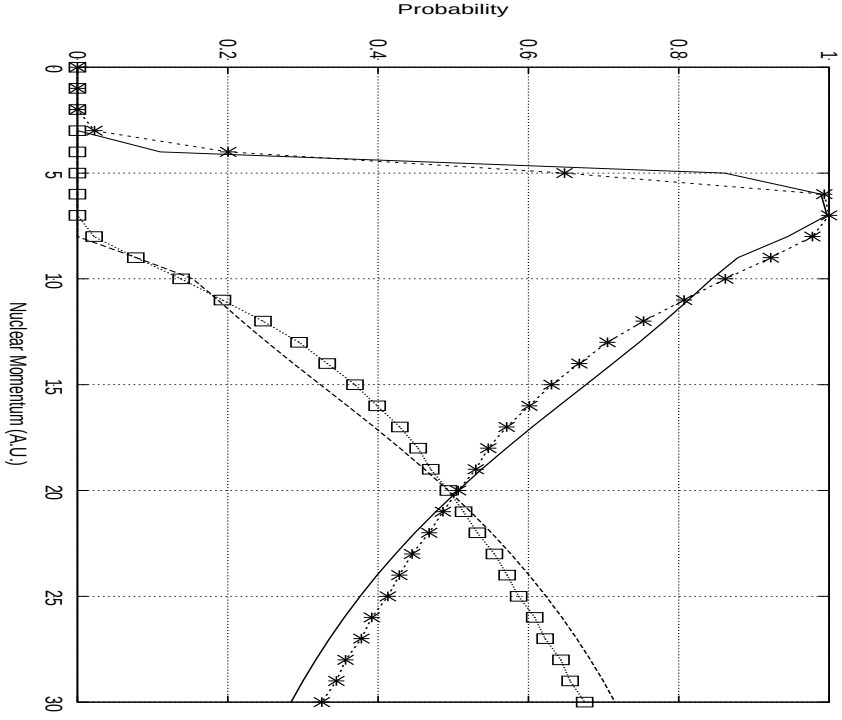
[Plotted $H_{11}(R)$, $H_{22}(R)$ plus adiabats: $E_1(R)$ and $E_2(R)$]

Results for Test Models

Single avoided crossing

$T_{1\leftarrow 1}, T_{2\leftarrow 1}$ (□, ✳, SQC with $\gamma = 0.366$)

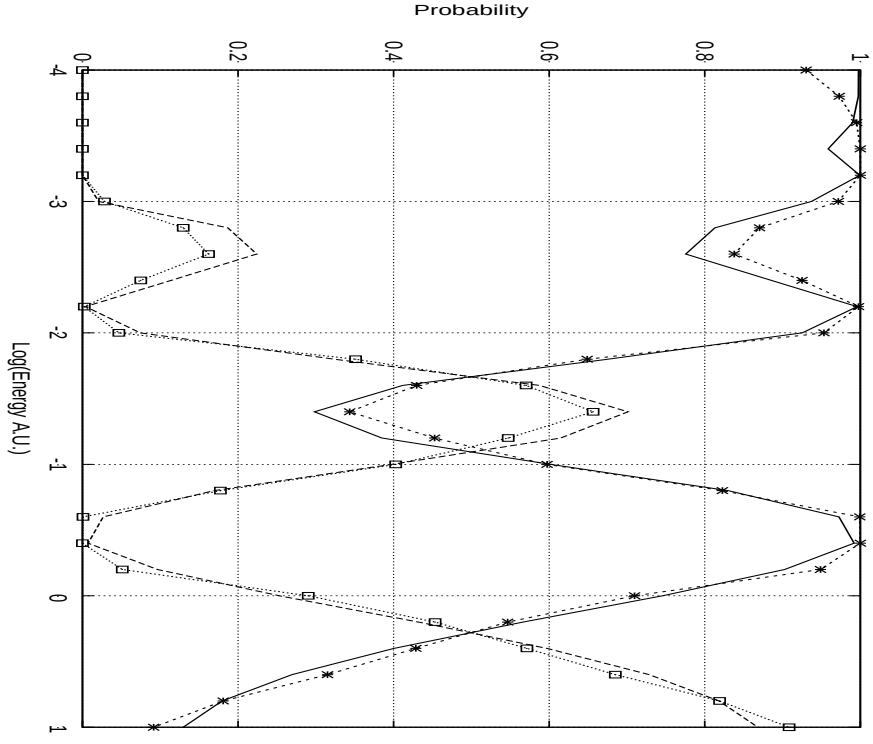
QM (solid and dashed lines)



Dual avoided crossing

$T_{1\leftarrow 1}, T_{2\leftarrow 1}$ (✳, □, SQC with $\gamma = 0.366$)

QM (solid and dashed lines)



Spin-Boson Model of Condensed Phase Non-Adiabatic Dynamics

The Model

$$H_{11}(\boldsymbol{Q}) = V_0(\boldsymbol{Q}) + V_1(\boldsymbol{Q}) + \epsilon$$

$$H_{22}(\boldsymbol{Q}) = V_0(\boldsymbol{Q}) - V_1(\boldsymbol{Q}) - \epsilon$$

$$H_{12}(\boldsymbol{Q}) = H_{21}(\boldsymbol{Q}) = \Delta$$

where $V_0(\boldsymbol{Q})$ represents a bath of oscillators

$$V_0(\boldsymbol{Q}) = \sum_{k=1}^{F} \frac{1}{2} m_k \, \omega_k^2 \, Q_k^2$$

shifted by $V_1(\boldsymbol{Q})$

$$V_1(\boldsymbol{Q}) = \sum_{k=1}^{F} c_k \, Q_k$$

with the coupling parameters $\{c_k\}$ chosen according to the relation

$$J(\omega) = \frac{\pi}{2} \sum_{k=1}^{F} \frac{c_k^2}{m_k \, \omega_k} \, \delta(\omega - \omega_k)$$

so that the bath frequencies $\{\omega_k\}$ are distributed according to the spectral density

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

Specific Calculations

Calculated the population difference, $D(t) = P_{1\leftarrow 1}(t) - P_{2\leftarrow 1}(t)$, using the SQC method, in each instance, with $\gamma = 0.366$

4 Cases:

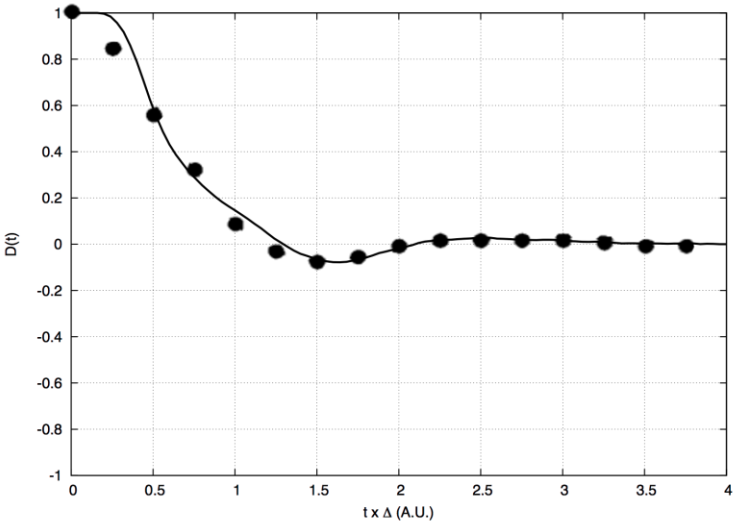
- Symmetric ($\epsilon = 0$) at High Temp: $\beta\Delta = 0.1, \alpha = 0.09, \omega_c/\Delta = 2.5$
- Symmetric ($\epsilon = 0$) at Low Temp: $\beta\Delta = 5, \alpha = 0.09, \omega_c/\Delta = 2.5$
- Asymmetric ($\epsilon = 1$) at Low Temp: $\beta\Delta = 5, \alpha = 0.1, \omega_c/\Delta = 2.5$
- Asymmetric ($\epsilon = 1$) at High Temp: $\beta\Delta = 0.25, \alpha = 0.1, \omega_c/\Delta = 1$

All show excellent agreement with the exact QM results. [Note: $\lim_{t\to\infty} D(t) \neq 0$, for the asymmetric low temp case.]

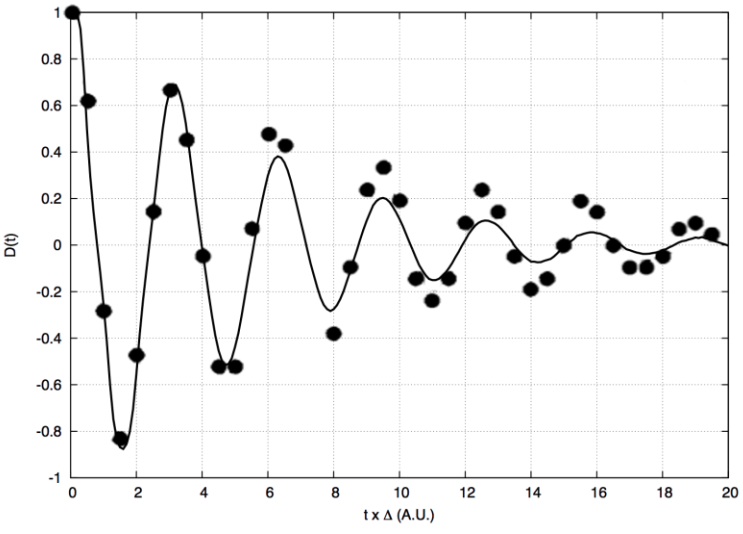
Spin-Boson Results

SQC, *γ=0.366* (solid line)
versus QM (dots)

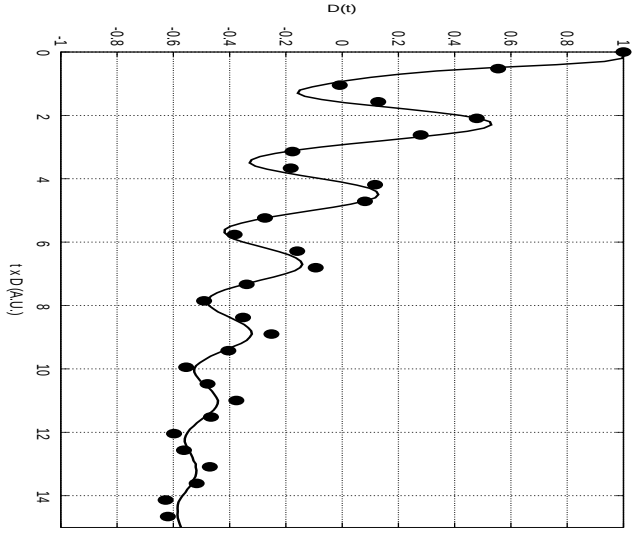
Symmetric, High Temp



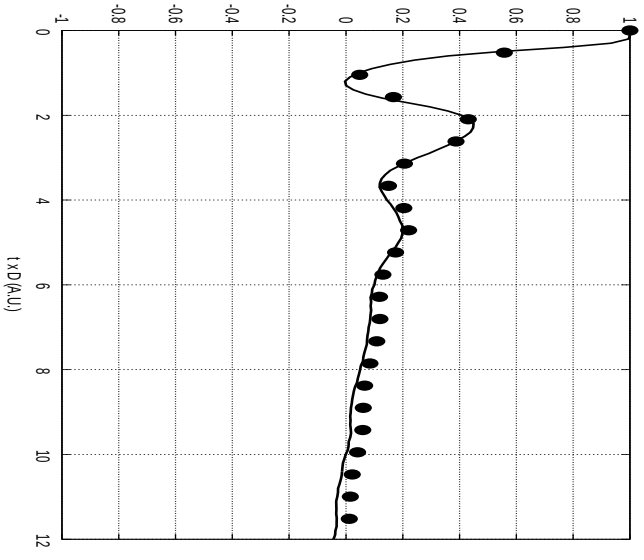
Symmetric Low Temp



Asymmetric, Low Temp



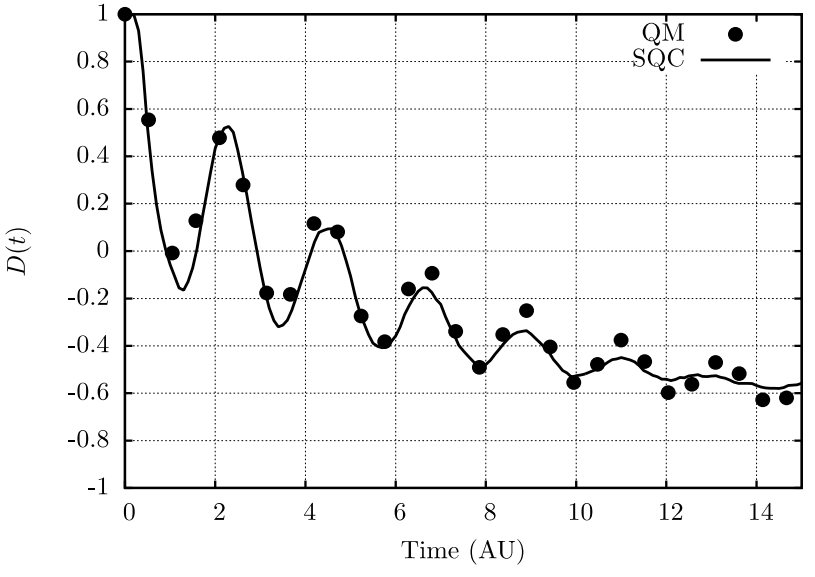
Asymmetric, High Temp



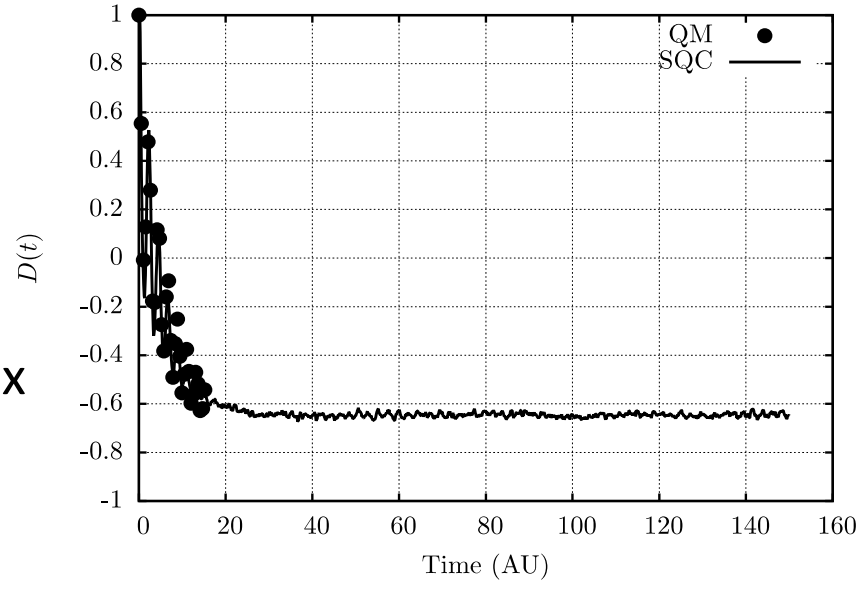
Example: Full Classical MM/SQC MD Simulation versus Full QM Result

- Asymmetric spin-boson problem ( ) at low temperature (weak coupling)

$\Delta E = \epsilon_2 - \epsilon_1 \neq 0$



"Coherent" decay to equilibrium distribution



Same, but with 10x timescale

Detailed Balance

(see Miller & Cotton, JCP 142 131103 (2015)

- Easy to show that the MM/SQC model provides a good description of detailed balance (DB)
- Consider a simple model of two electronic states having energies ε_1 and ε_2 (independent of nuclear coordinates), coupled to a classical stochastic bath at temperature *T* (which drives the electronic states to Boltzmann equilibrium as $t \to \infty$)
  - The DB condition is therefore:

$$\frac{P_2}{P_1} = e^{-(\epsilon_2 - \epsilon_1)/kT} \tag{1}$$

  - This model was used by Tully et al. (JCP, 2006) to demonstrate how surface hopping (SH) treats DB, the primary conclusions from this prior work being that:
    1) "Surface hoping" does a good job of describing Eq. (1) correctly
    2) "Ehrenfest dynamics" gives a probability distribution of the final electronic action variables as

$$P(n_1, n_2) \propto \exp\left(-n_1\epsilon_1/kT - n_2\epsilon_2/kT\right) \tag{2}$$

    which when used in the standard/traditional Ehrenfest way, i.e.

$$\frac{P_2}{P_1} = \frac{\langle n_2 \rangle}{\langle n_1 \rangle} \ ,$$

    gives a very poor description of detailed balance

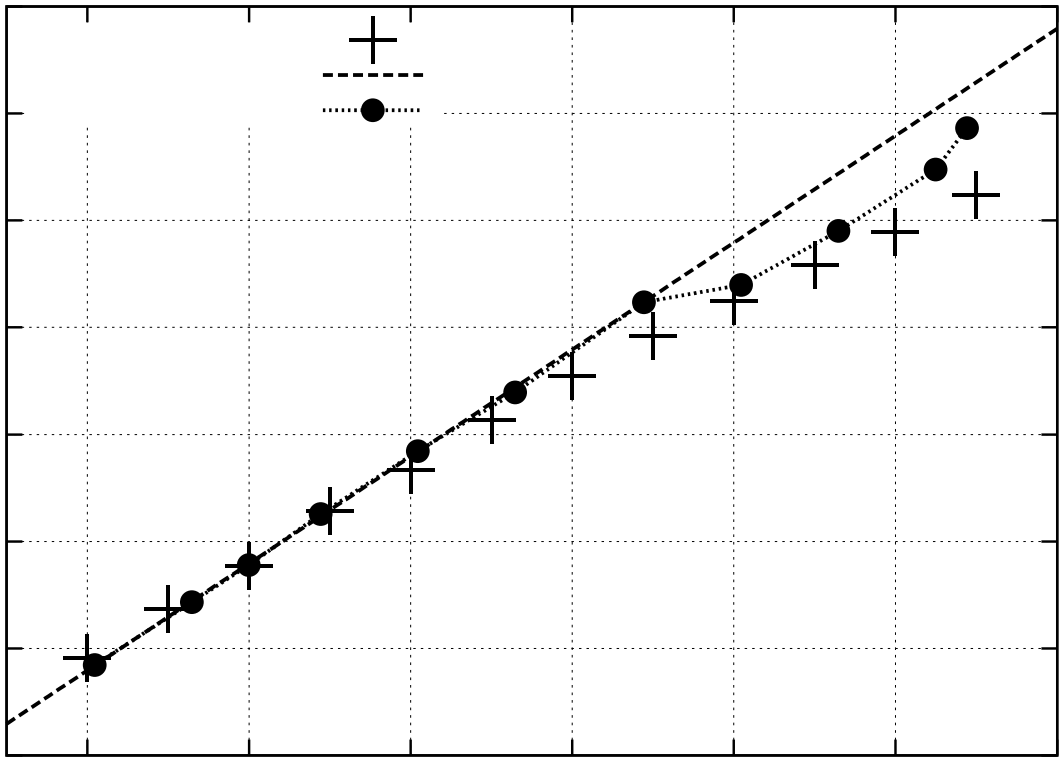
Detailed Balance (con't)

- But when the electronic populations which result from "Ehrenfest Dynamics" (Eq. (2)) are "processed" quasi-classically (standard QCT, SQC, or otherwise)—e.g., by using a histogram "box" windowing function of width γ—one obtains

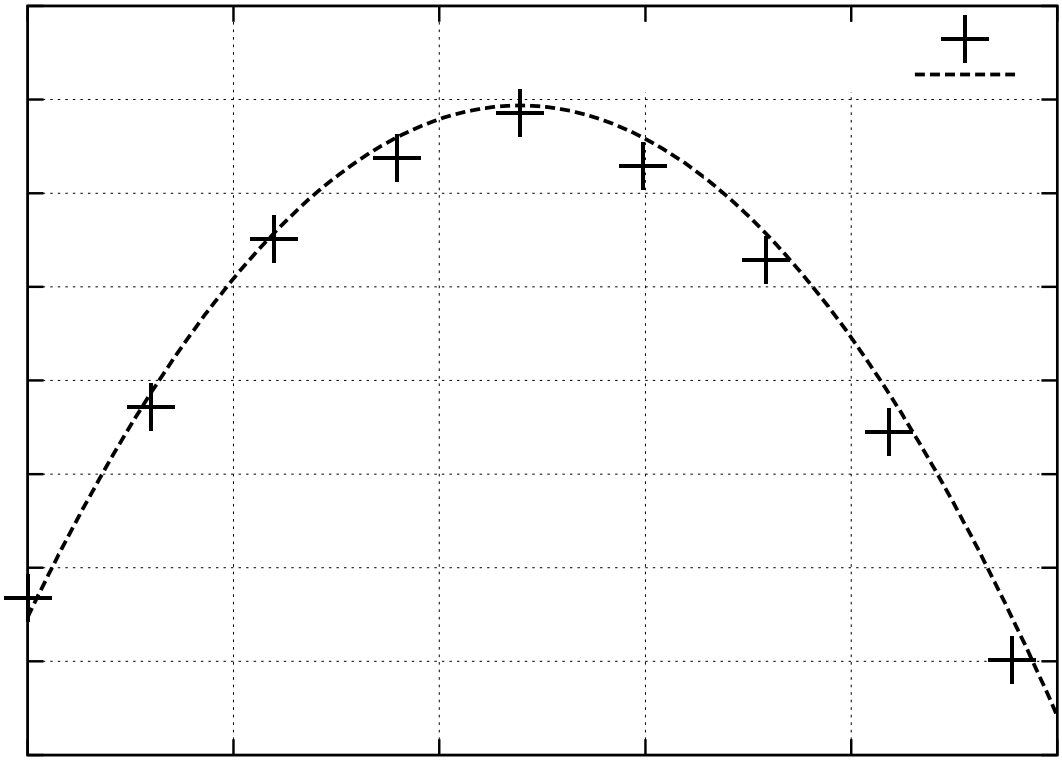
$$\frac{P_2}{P_1} = \int_{-\gamma}^{\gamma} dn_1 \int_{1-\gamma}^{1+\gamma} dn_2 \; P(n_1, n_2) \Big/ \int_{1-\gamma}^{1+\gamma} dn_1 \int_{-\gamma}^{\gamma} dn_2 \; P(n_1, n_2) = \frac{e^{-\epsilon_2/kT}}{e^{-\epsilon_1/kT}}$$

i.e., the correct DB condition of Eq. (1) independent of γ !

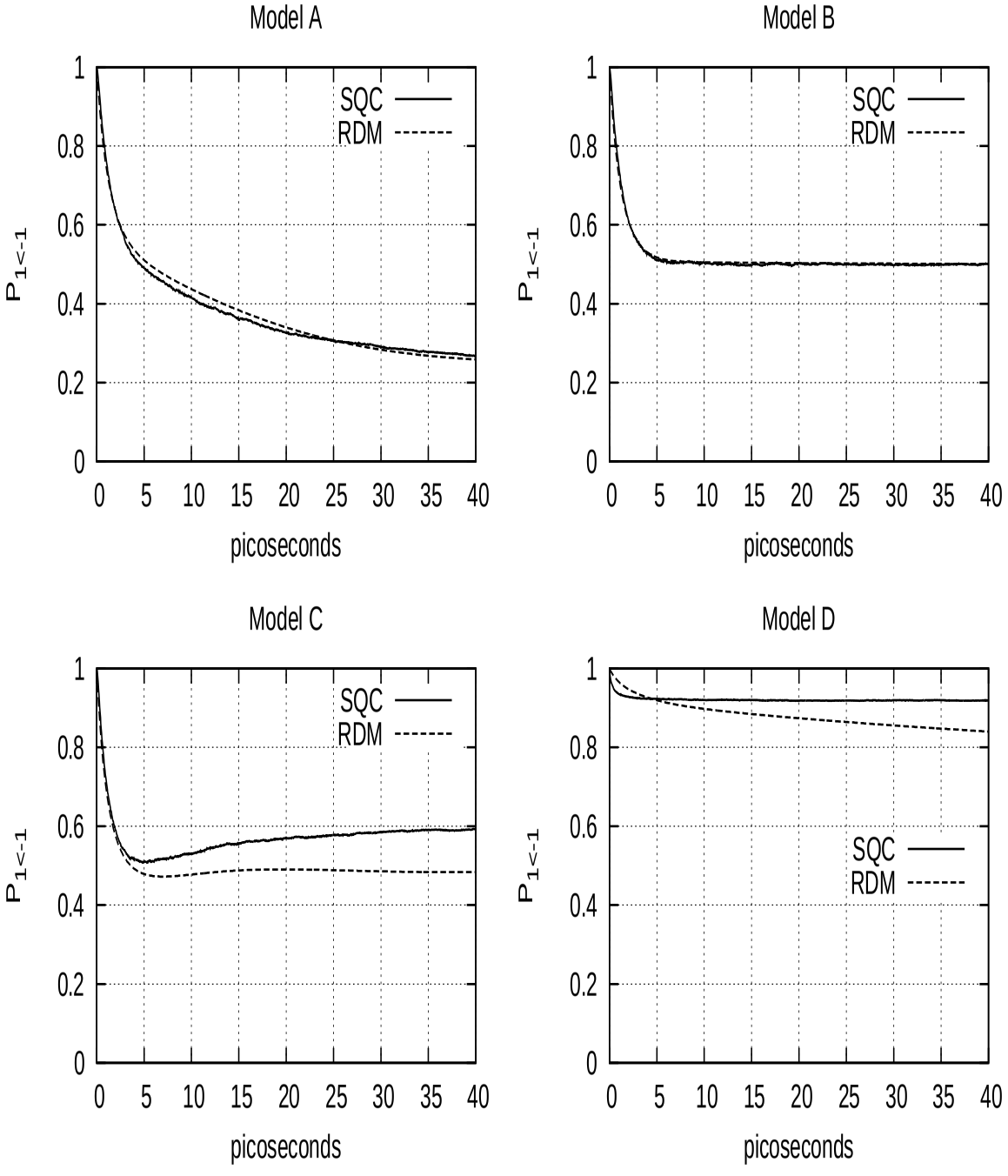
- And it turns out that this holds for *any* appropriate windowing function (Gaussians, histogram boxes, etc.), so long as the same windowing function is applied to each of the applicable final electronic states



βΔ

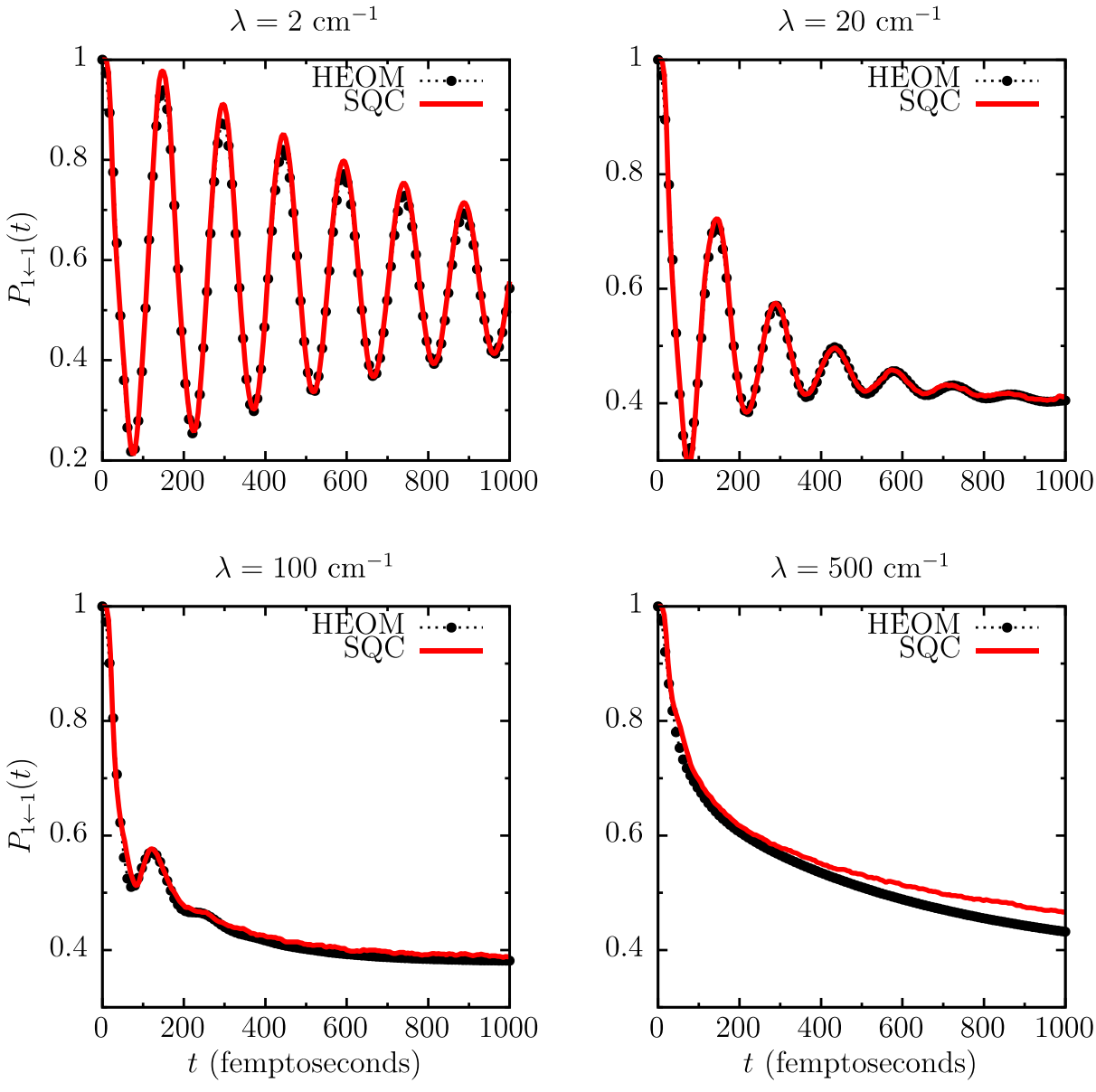


ε λ


Model A
Model B
Model C
Model D
SQC
RDM
$P_{1<-1}$
picoseconds
0
0.2
0.4
0.6
0.8
1
0
5
10
15
20
25
30
35
40

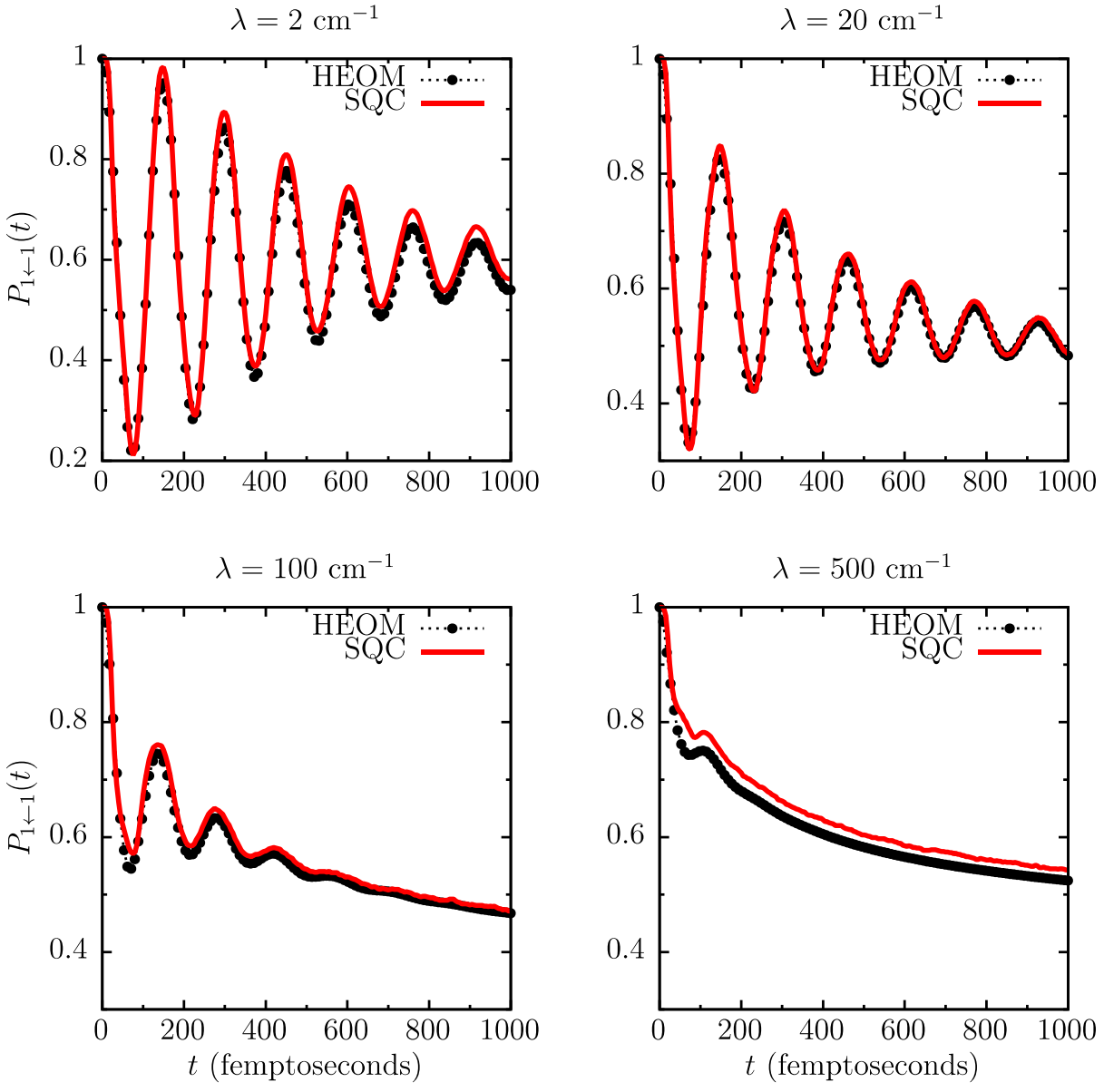
2-State Site-Exciton Model

$T = 300$ K, $\epsilon_1 - \epsilon_2 = J_{12} = 100$ cm^{-1}, $\omega_c = 53.08$ cm^{-1}

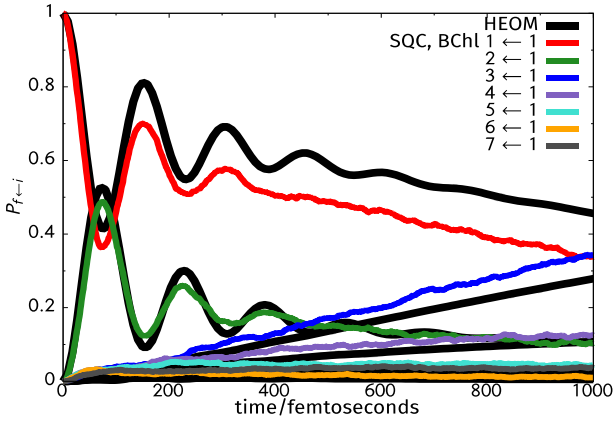


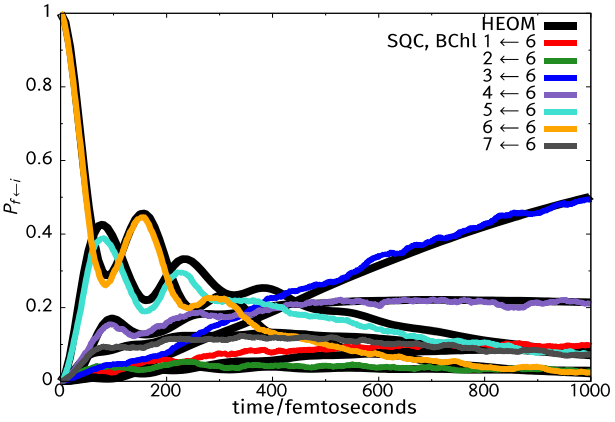
2-State Site-Exciton Model

Same parameters, except: $\omega_c = 10.61\ \mathrm{cm}^{-1}$

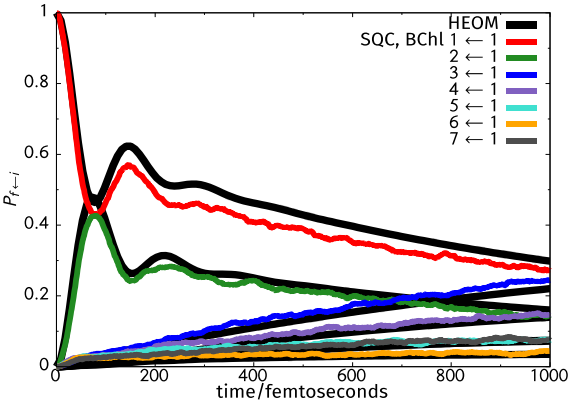


The 7-state FMO model (77K) (using the SQC triangle windows, generalized to arbitrary dimension)



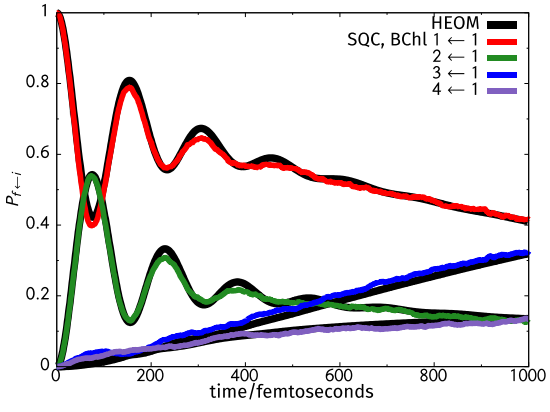


At 300K, the results are even better (indicating any issues are presumably nuclear QM effects):

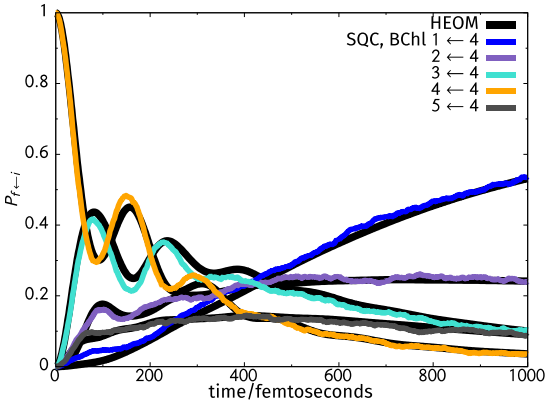


Also…

4-state model (77K)



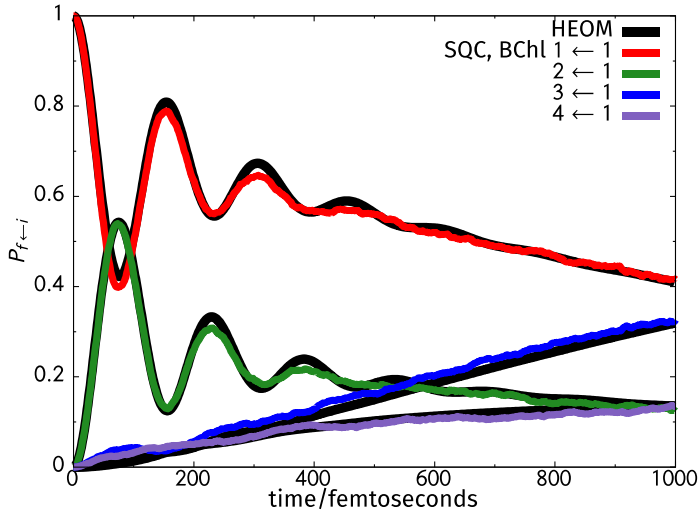
5-state model (77K)



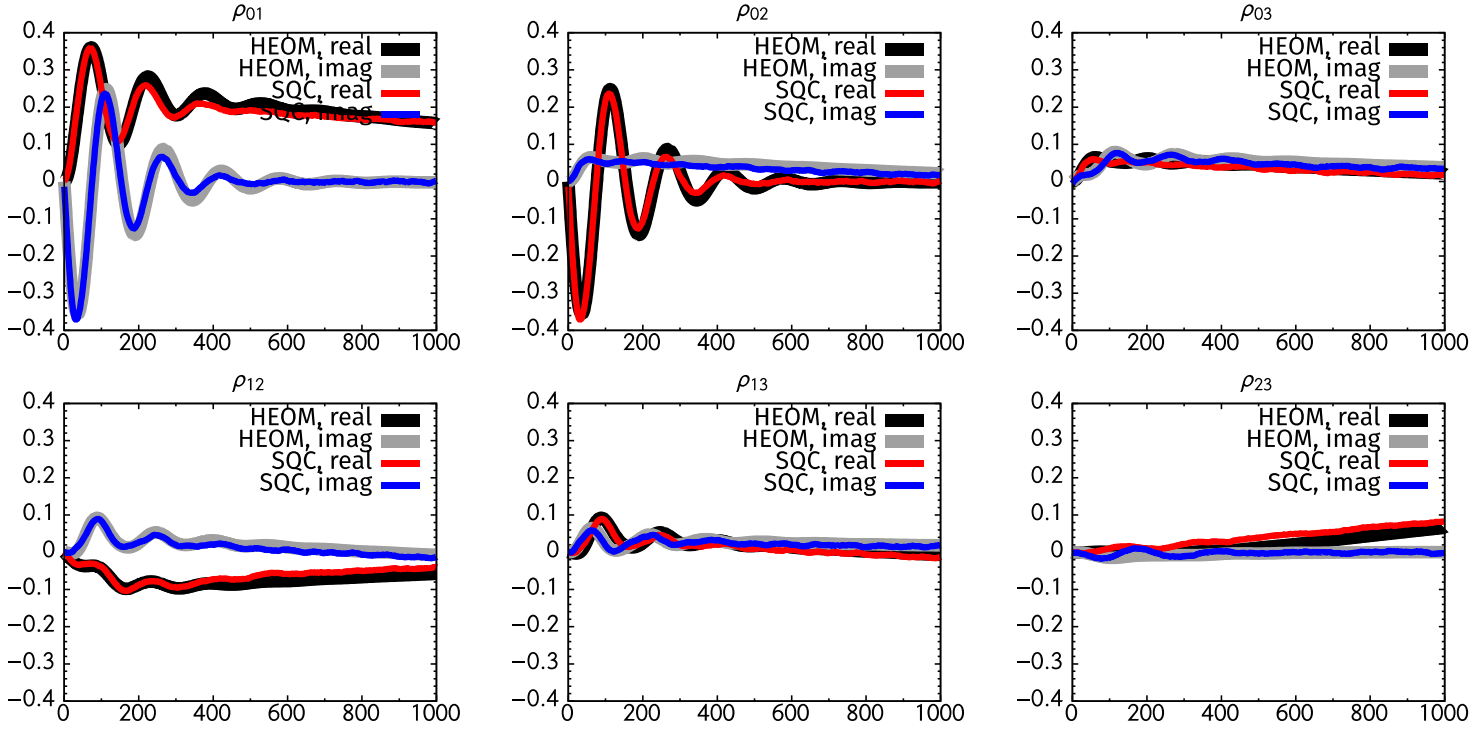
Note: These and All FMO calculations that follow use 10,000 trajectory ensembles

Full SQC density matrix

4-state FMO model

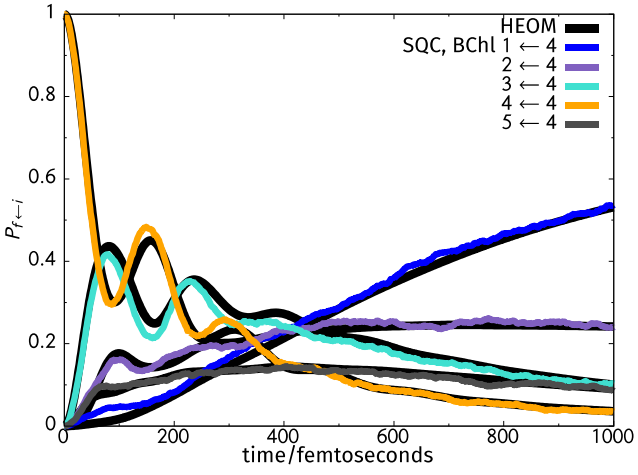


4-state version of the FMO problem, SQC density matrix (optimized)

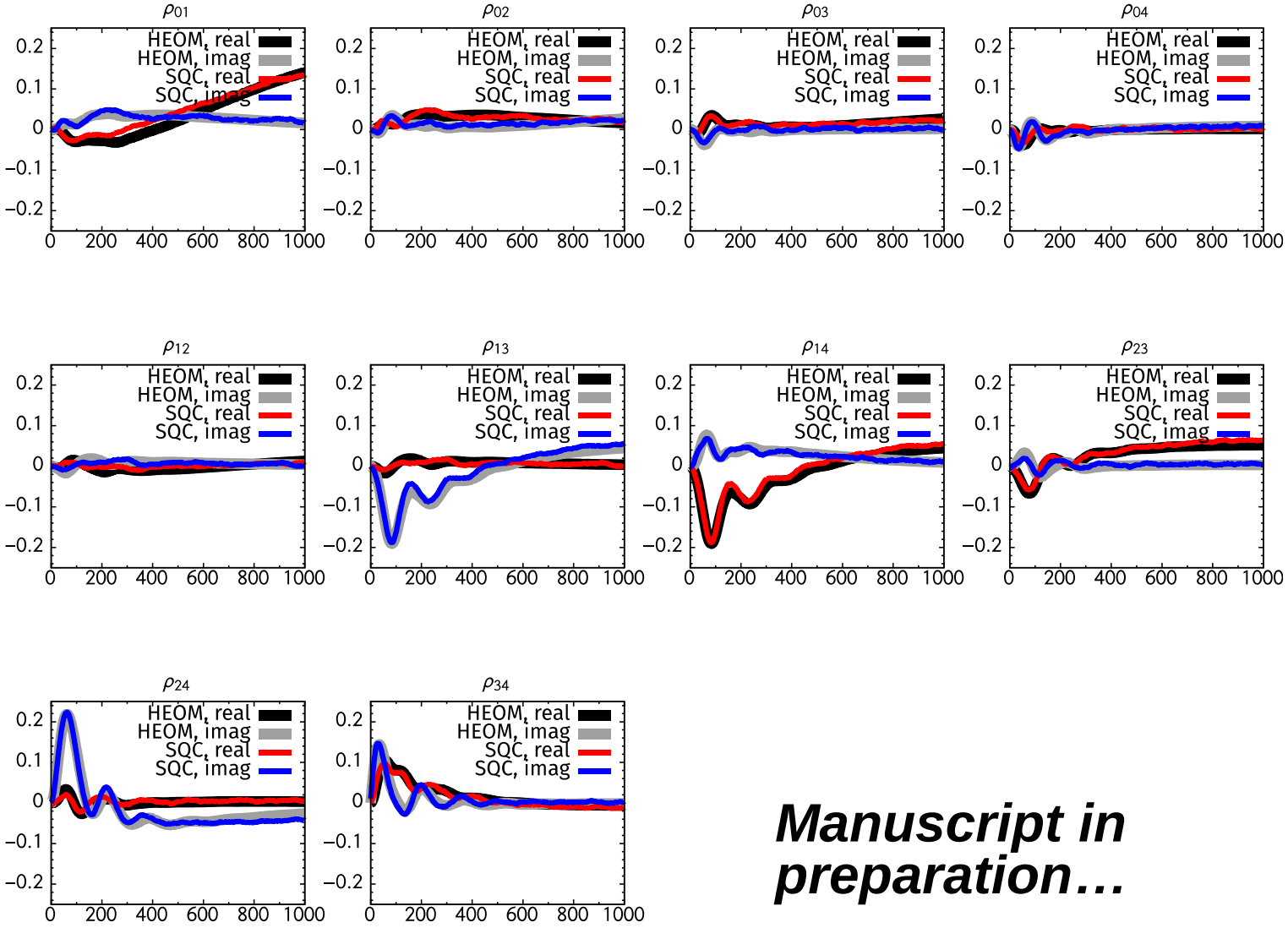


Full SQC density matrix calculations (con't)

5-state FMO model



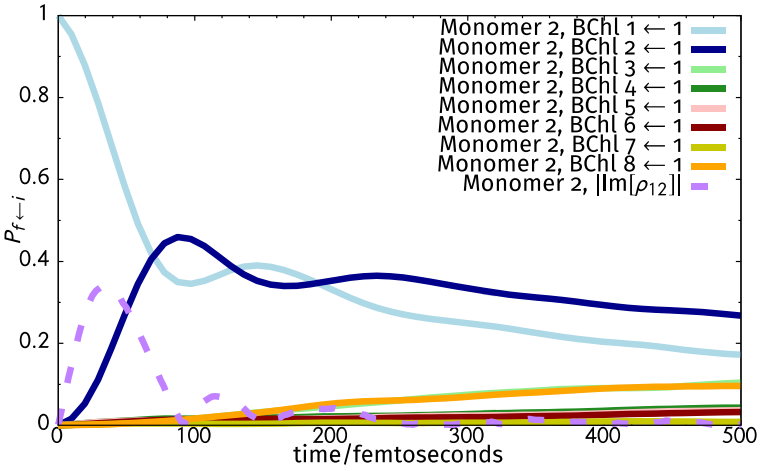
5-state version of the FMO problem, SQC density matrix (optimized)

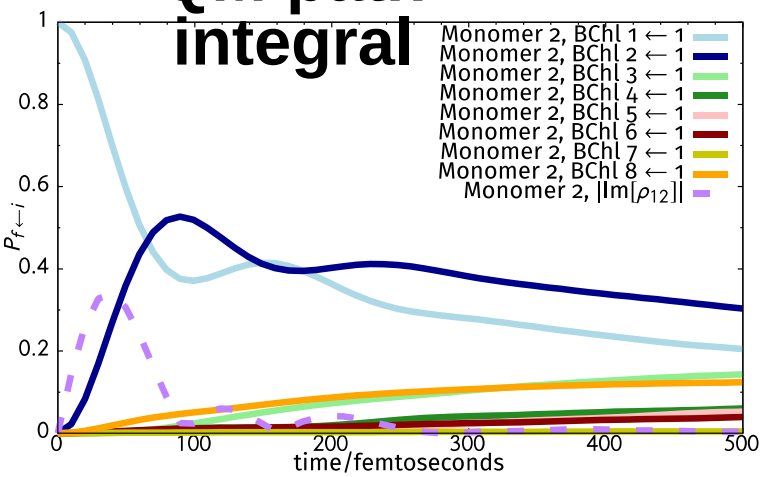


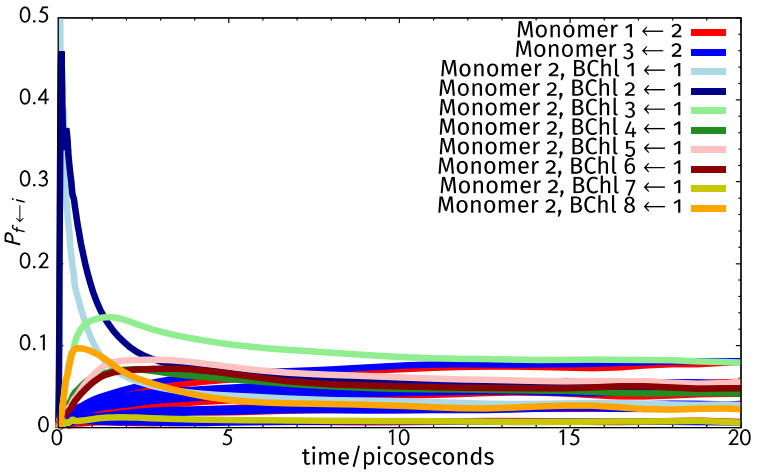
Manuscript in preparation…

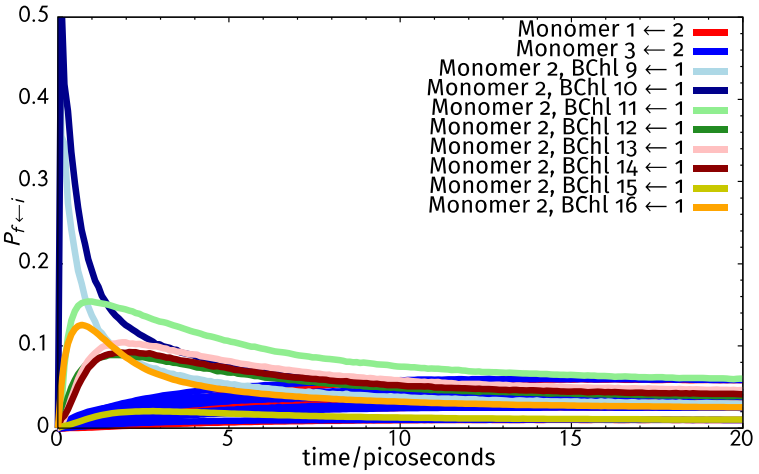
24 Pigment/State FMO *Trimer*

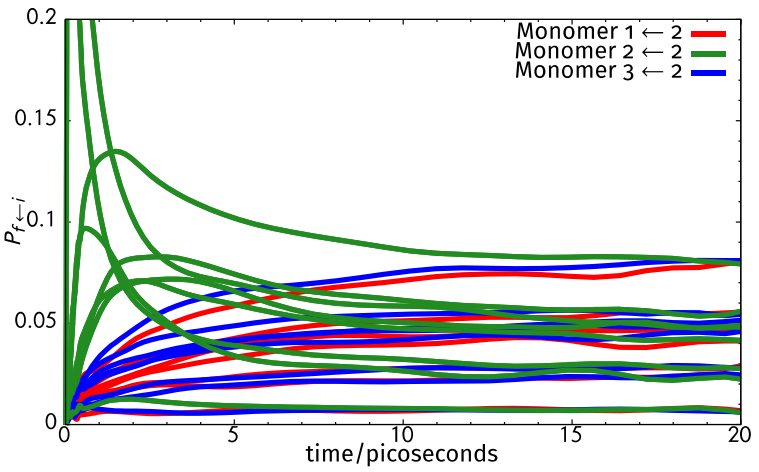
QM path integral











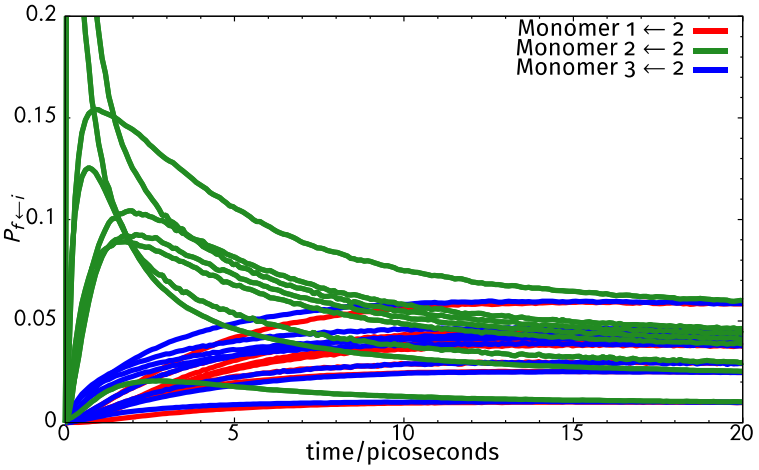


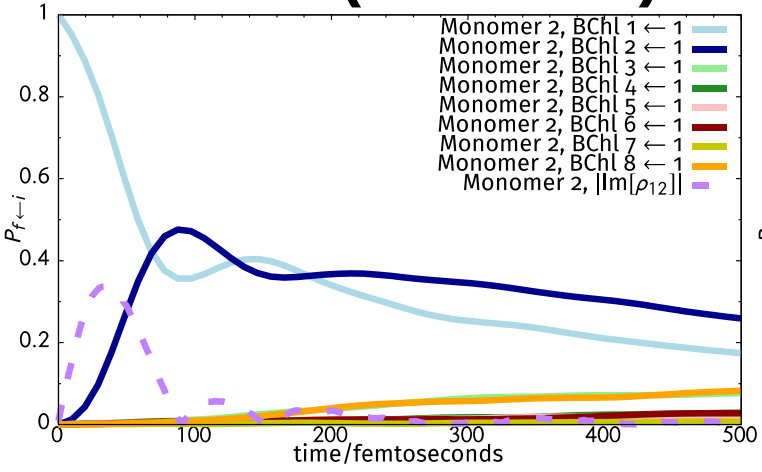
TABLE II. Approximate relative *single processor* compute costs to 20 picoseconds for 24-state FMO trimer dynamics

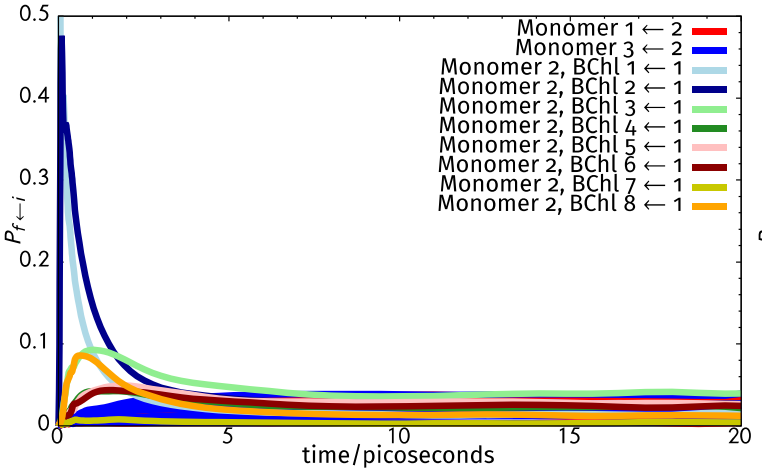
	QM path integral[a]	SQC/MM[b]
Core-seconds	4,928,000	10,000
Wall-time (16-core processor)	≈ 3-4 days	≈ 10 minutes
Relative cost	100%	≈ 0.2%

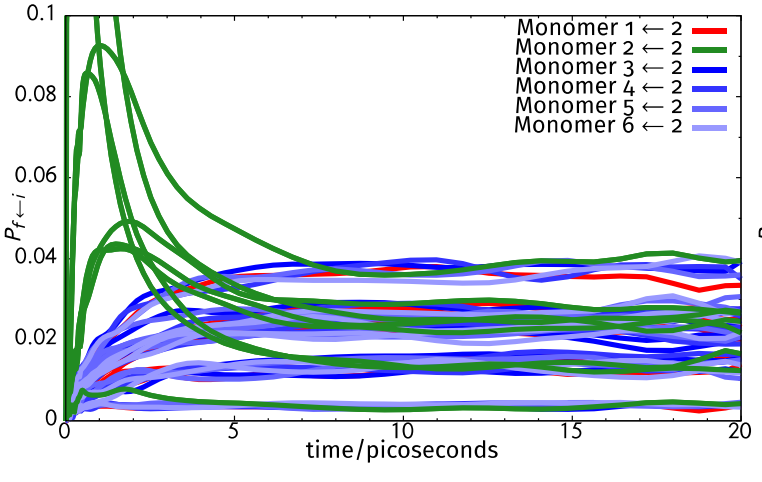
Demonstrative treatment of more states

(SQC triangle windows, generalized)

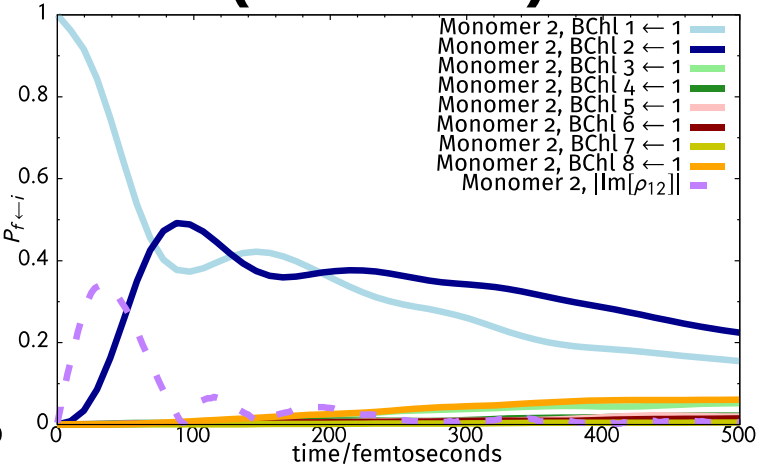
48 Pigments/States FMO *Hexamer* model (fictitious)

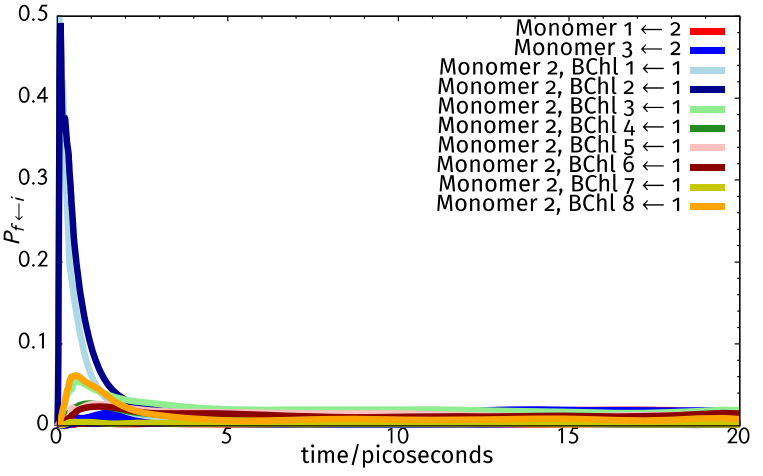


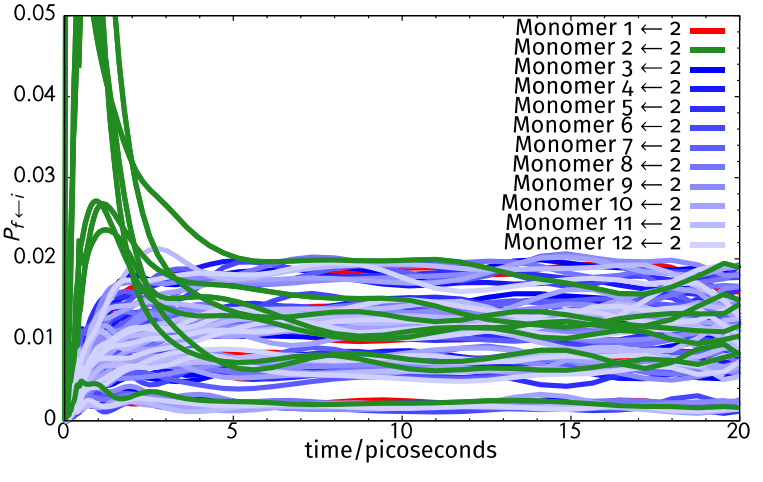




96 Pigments/States FMO *Dodecamer* model (fictitious)







Cf. **adiabatic representation**

$$H(\mathbf{x},\mathbf{p},\mathbf{R},\mathbf{P}) = \frac{1}{2\mu}(\mathbf{P}+\mathbf{\Delta P})^2 + \sum_i^F \left(\tfrac{1}{2}p_i^2 + \tfrac{1}{2}x_i^2 - \gamma\right) \underbrace{E_i(\mathbf{R})}_{\text{B.O. PES}}$$

where

$$\mathbf{\Delta P}(\mathbf{x},\mathbf{p},\mathbf{R}) = \sum_{i<j}(x_i p_j - x_j p_i) \underbrace{\left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle}_{\substack{\text{non-adibatic} \\ \text{couplings}}}$$

(i.e., a vector potential coupling analogous to that for a molecule in an E&M field)

Hamilton's equations:

$$\dot{x}_i = \frac{\partial H}{\partial p_i} = p_i\, E_i(\mathbf{R}) + \sum_j^F x_j \left\langle \phi_j \middle| \frac{\partial \phi_i}{\partial \mathbf{R}} \right\rangle \cdot \frac{\mathbf{P}+\mathbf{\Delta P}}{\mu} \tag{1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial x_i} = -x_i\, E_i(\mathbf{R}) + \sum_j^F p_j \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle \cdot \frac{\mathbf{P}+\mathbf{\Delta P}}{\mu} \tag{2}$$

$$\dot{\mathbf{R}} = \frac{\partial H}{\partial \mathbf{P}} = \frac{\mathbf{P}+\mathbf{\Delta P}}{\mu} \tag{3}$$

$$\begin{aligned} \dot{\mathbf{P}} = -\frac{\partial H}{\partial \mathbf{R}} &= -\sum_i \left(\tfrac{1}{2}p_i^2 + \tfrac{1}{2}x_i^2 - \gamma\right) \frac{\partial E_i}{\partial \mathbf{R}} \\ &\quad - \sum_{ij} x_i p_j \frac{\partial}{\partial \mathbf{R}} \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle \cdot \frac{\mathbf{P}+\mathbf{\Delta P}}{\mu} \end{aligned} \tag{4}$$

But, the EOM for $\dot{\mathbf{P}}$ (Eq. (4)) involves

$$\frac{\partial}{\partial \mathbf{R}} \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle = \left\langle \frac{\partial \phi_i}{\partial \mathbf{R}} \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle + \left\langle \phi_i \middle| \frac{\partial^2 \phi_j}{\partial \mathbf{R}^2} \right\rangle$$

just as does the QM Schrödinger Eq.

Kinematic (adiabatic) EOM

The solution is to work in terms of *"kinematic"* momenta:

$$\mathbf{P}_{\text{kin}} \equiv \mathbf{P} + \mathbf{\Delta P} \qquad \text{(i.e., } \mathbf{P}_{\text{kin}} = \mu\dot{\mathbf{R}}\text{, from Eq. (4c))}.$$

Differentiating it gives:

$$\begin{aligned}\dot{\mathbf{P}}_{\text{kin}} &= \dot{\mathbf{P}} + \frac{d}{dt}\mathbf{\Delta P}(\mathbf{x}, \mathbf{p}, \mathbf{R}) \\ &= \underbrace{-\sum_i \left(\tfrac{1}{2}p_i^2 + \tfrac{1}{2}x_i^2 - \gamma\right)\frac{\partial E_i}{\partial \mathbf{R}} - \cancel{\frac{\partial \mathbf{\Delta P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}}}}_{\text{Eq. (4d) for } \dot{\mathbf{P}}} + \overbrace{\frac{\partial \mathbf{\Delta P}}{\partial \mathbf{x}} \cdot \dot{\mathbf{x}} + \frac{\partial \mathbf{\Delta P}}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}} + \cancel{\frac{\partial \mathbf{\Delta P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}}}}^{\text{the chain rule}}.\end{aligned}$$

where the terms involving $\frac{\partial}{\partial \mathbf{R}} \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle$ are seen to cancel!!!

And after some more algebra (and inserting $\dot{x}_i$ and $\dot{p}_i$ from Eqs. (4a) and (4b)) gives

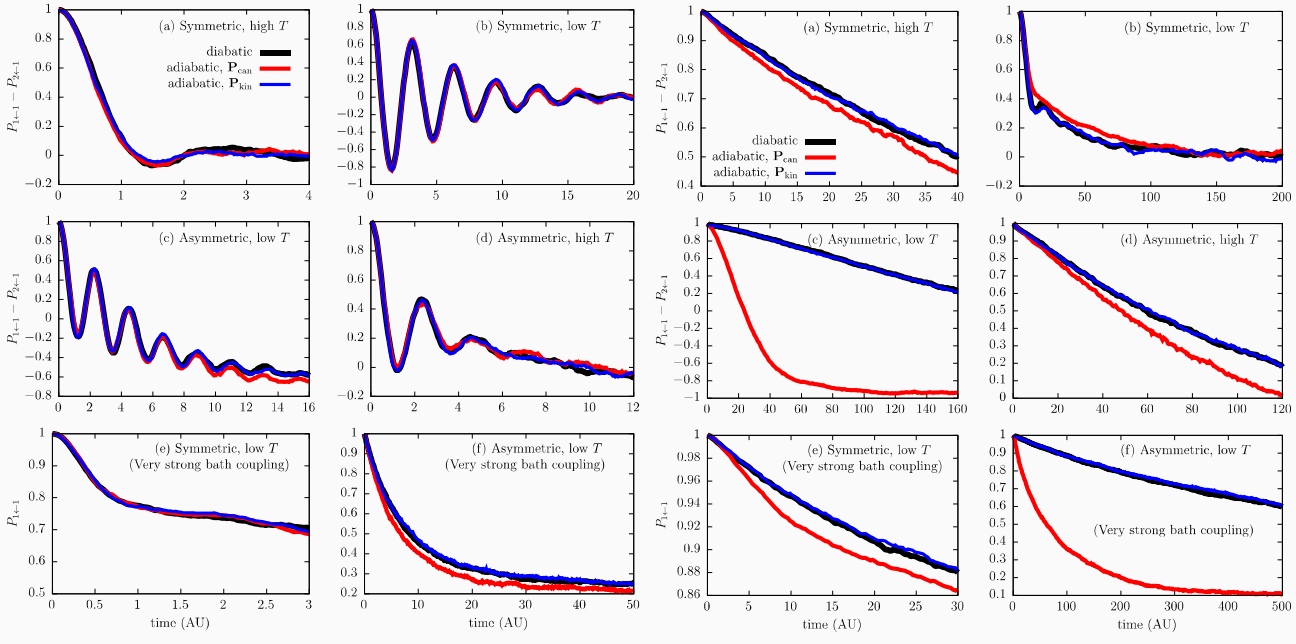
$$\dot{\mathbf{P}}_{\text{kin}} = -\sum_i \left(\tfrac{1}{2}p_i^2 + \tfrac{1}{2}x_i^2 - \gamma\right)\frac{\partial E_i}{\partial \mathbf{R}} - \sum_{i<j} \left(\tfrac{1}{2}p_i p_j + \tfrac{1}{2}x_i x_j\right)\left(E_j(\mathbf{R}) - E_i(\mathbf{R})\right)\left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle \tag{4d'}$$

which is the final EOM for $\mathbf{P}_{\text{kin}}$ which still depends on $\mathbf{d}_{ij}$ but *does not* explicitly depend on second-derivative coupling terms (e.g., $\mathbf{D}_{ij}$).

Spin-boson benchmarks (revisited)

But, the second-derivative couplings are *still* accounted for (without having to calculate them), and sometimes their effect can be substantial:

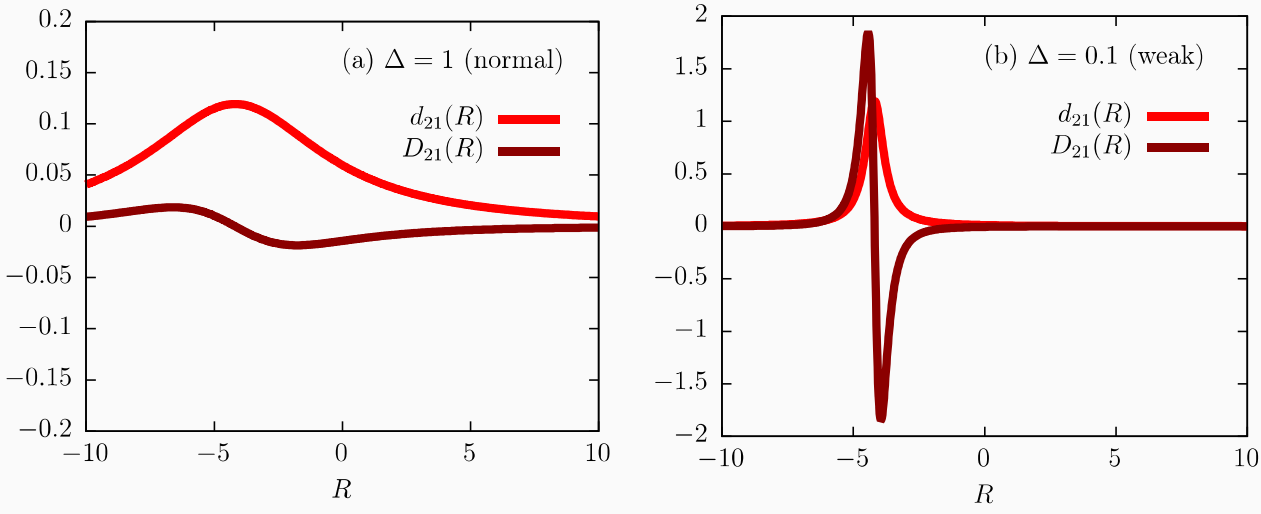
Non-adiabatic coupling $\Delta = 1$ $\qquad$ $\Delta = 10\%$ ($10\times$ timescale)



SQC/MM diabatic v. adiabatic spin-boson[2] calculations (triangle windowing scheme) using Eq. (4d) (neglecting $\frac{\partial}{\partial \mathbf{R}} \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial \mathbf{R}} \right\rangle$ terms) or Eq. (4d′) (integrating $\dot{\mathbf{P}}_{\text{kin}}$)

[2] Same six benchmarks from Bill's talk

$\mathbf{d}_{ij}$ versus $\mathbf{D}_{ij}$



Sample first- and second-derivative couplings corresponding to spin-boson version (c) shown on earlier slide[3]

[3] The chosen R coordinate is the harmonic bath mode with the strongest coupling.

Energy conservation

Note: the conserved energy in terms of $\mathbf{P}_{\text{kin}}$ is given simply by

$$E_{\text{tot}}(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}_{\text{kin}}) = \frac{1}{2\mu}\mathbf{P}_{\text{kin}}^2 + \sum_i \left(\tfrac{1}{2}p_i^2 + \tfrac{1}{2}x_i^2 - \gamma\right) E_i(\mathbf{R}), \tag{5}$$

which is just the adiabatic MM Hamiltonian with the substitution $\mathbf{P} + \mathbf{\Delta P} \to \mathbf{P}_{\text{kin}}$.

- This must be true, because the "kinematic" adiabatic EOM are totally equivalent to the original adiabatic EOM (so long as all terms are kept).
- **But**, Eq. (5) is **NOT** a Hamiltonian (and there is none for the kinematic EOM).

If Hamilton's Equations were applied to Eq. (5), the resulting EOM would have no electronic transitions!

Cf. conical intersection, 2-state case

Recall the term in the EOM for the "kinematic" momentum,

$$\dot{\mathbf{P}}_{\text{kin}} \sim \big(E_2(\mathbf{R}) - E_1(\mathbf{R})\big) \left\langle \psi_2 \middle| \frac{\partial \psi_1}{\partial \mathbf{R}} \right\rangle \quad \equiv (*)$$

In terms of the mixing angle,

$$\begin{aligned} \left\langle \psi_2 \middle| \frac{\partial \psi_1}{\partial \mathbf{R}} \right\rangle &= \frac{1}{2} \frac{\partial}{\partial \mathbf{R}} \tan^{-1}\left(\frac{2H_{12}(\mathbf{R})}{\Delta H(\mathbf{R})} \right) \qquad \text{where} \quad \Delta H = H_{22} - H_{11} \\ &= \frac{1}{\Delta H^2 + 4\, H_{12}^2} \left(\Delta H \frac{\partial H_{12}}{\partial \mathbf{R}} - H_{12} \frac{\partial \Delta H}{\partial \mathbf{R}} \right). \end{aligned}$$

We also have

$$E_2(\mathbf{R}) - E_1(\mathbf{R}) = \sqrt{\Delta H^2 + 4 H_{12}^2},$$

and near a conical intersection,

$$\Delta H(\mathbf{R}) \simeq 0 + \mathbf{a} \cdot \mathbf{R}$$

$$H_{12}(\mathbf{R}) \simeq 0 + \mathbf{b} \cdot \mathbf{R}.$$

$$\implies \qquad (*) = \frac{\mathbf{b}\,(\mathbf{a}\cdot\mathbf{R}) - \mathbf{a}\,(\mathbf{b}\cdot\mathbf{R})}{\sqrt{(\mathbf{a}\cdot\mathbf{R})^2 + 4\,(\mathbf{b}\cdot\mathbf{R})^2}}$$

and $\therefore$ with $\mathbf{R} = R\,\hat{\mathbf{R}}$,

$$= \frac{\mathbf{b}\,(\mathbf{a}\cdot\hat{\mathbf{R}}) - \mathbf{a}\,(\mathbf{b}\cdot\hat{\mathbf{R}})}{\sqrt{(\mathbf{a}\cdot\hat{\mathbf{R}})^2 + 4\,(\mathbf{b}\cdot\hat{\mathbf{R}})^2}} \quad \leftarrow \underline{\text{independent of } |\mathbf{R}|}$$

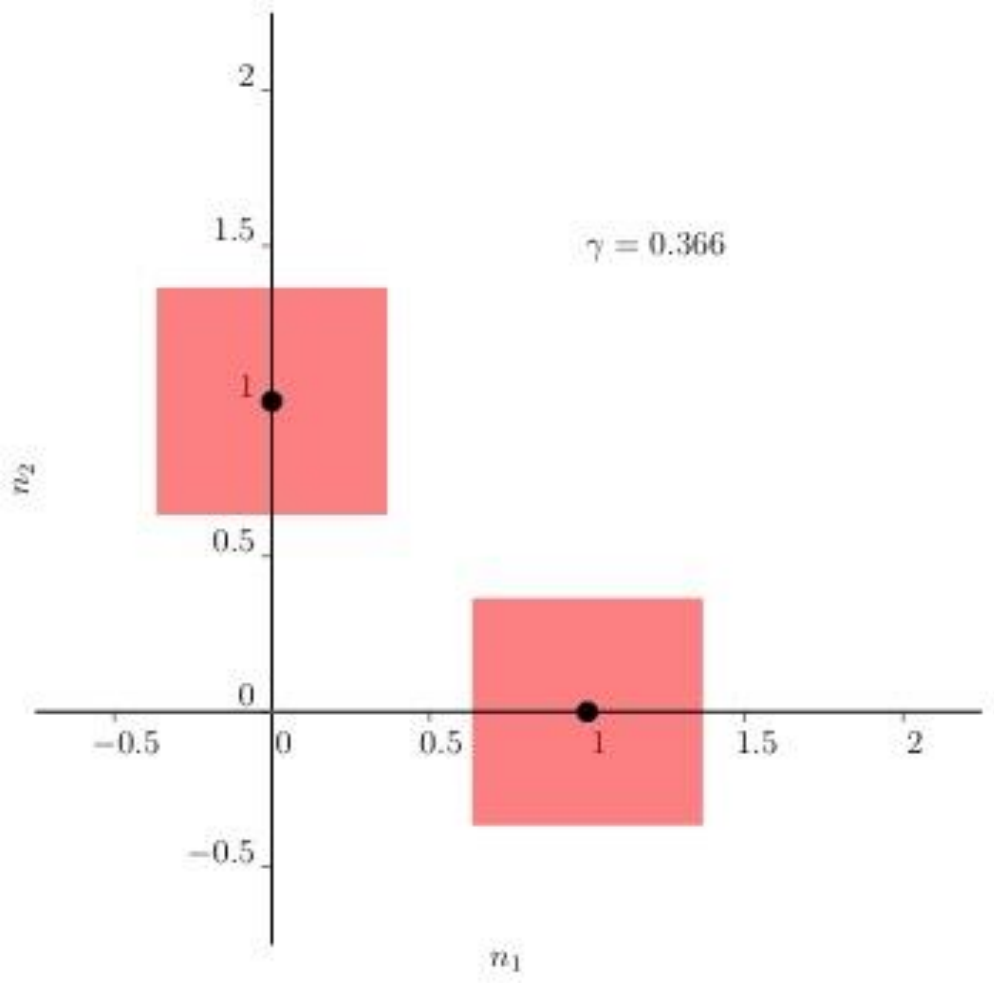
Also, about an <u>avoided</u> crossing:

$$\Delta H(\mathbf{R}) \simeq 0 + \mathbf{a} \cdot \mathbf{R}$$

$$H_{12}(\mathbf{R}) \simeq \text{const.}$$

$$\implies \qquad (*) = \frac{-H_{12}\,\mathbf{a}}{\sqrt{a^2 + 4\, H_{12}^2}}$$

Issues for Weak Coupling



Universal 2-Channel Scattering Example

A general 2-channel S-matrix may be written as:

$$\mathbf{S} = \begin{pmatrix} \sqrt{1-p}\, e^{i\alpha}, & i\,\sqrt{p} e^{i\,(\alpha+\beta)/2} \\ i\,\sqrt{p} e^{i\,(\alpha+\beta)/2}, & \sqrt{1-p}\, e^{i\,\beta} \end{pmatrix},$$

where the parameter p is the transition probability; i.e., $|S_{1,2}|^2 = p$. For a fixed nuclear trajectory, $\mathbf{R}(t)$, the electronic amplitudes are exactly equivalent to the classical action-angle variables as related by

$$c_k(t) = \sqrt{n_k(t)}\, e^{i\, q_k(t)} \qquad \therefore \qquad \begin{pmatrix} c_1(\infty) \\ c_2(\infty) \end{pmatrix} = \begin{pmatrix} S_{1,1} & S_{1,2} \\ S_{2,1} & S_{2,2} \end{pmatrix} \begin{pmatrix} c_1(0) \\ c_2(0) \end{pmatrix}.$$

Then we have

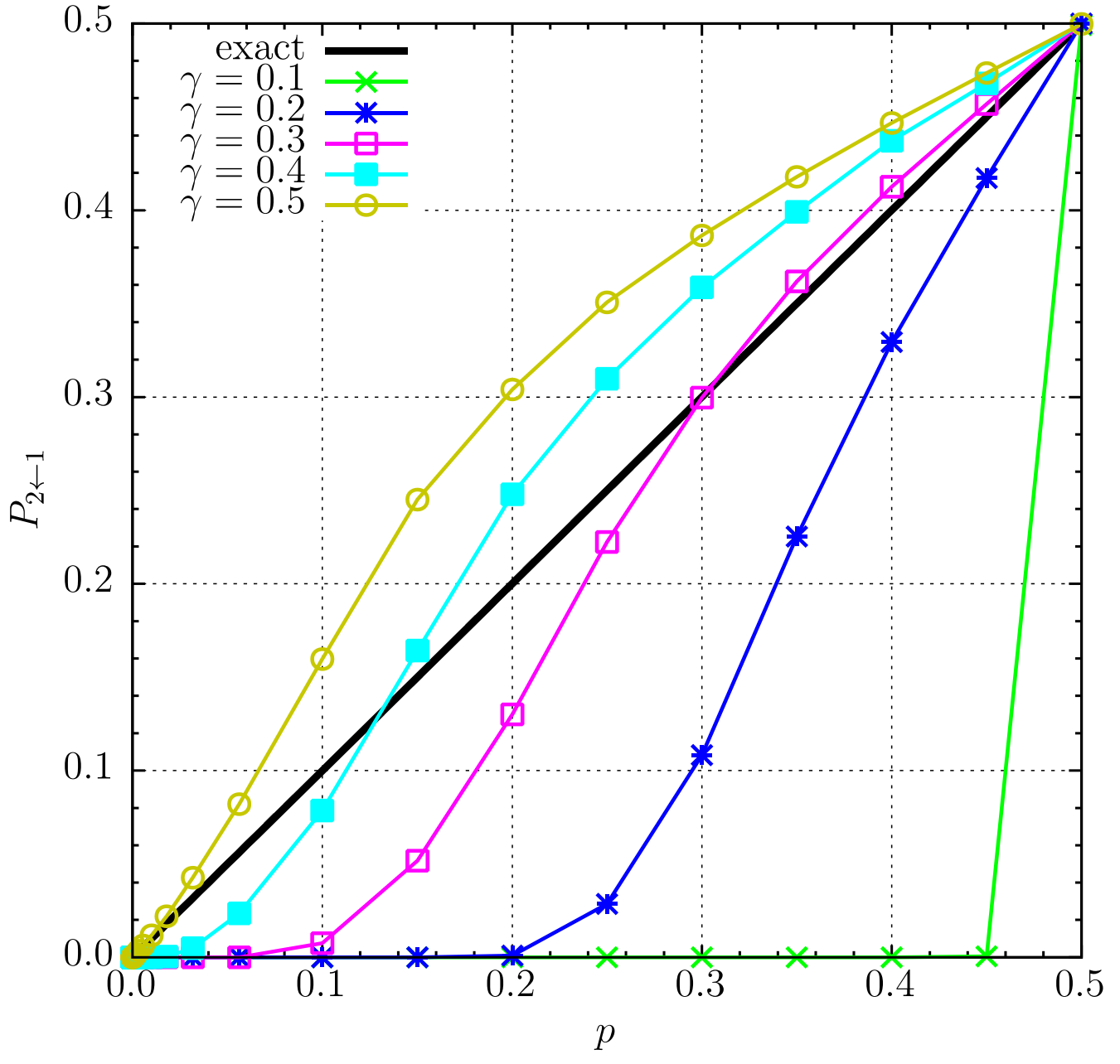
$$n_1(\infty) = (1-p)\, n_1(0) + p\, n_2(0) - 2\sqrt{p\,(1-p)}\sqrt{n_1(0)\, n_2(0)} \cdot \sin\left(q_2(0) - q_1(0) + \frac{\beta - \alpha}{2} \right)$$

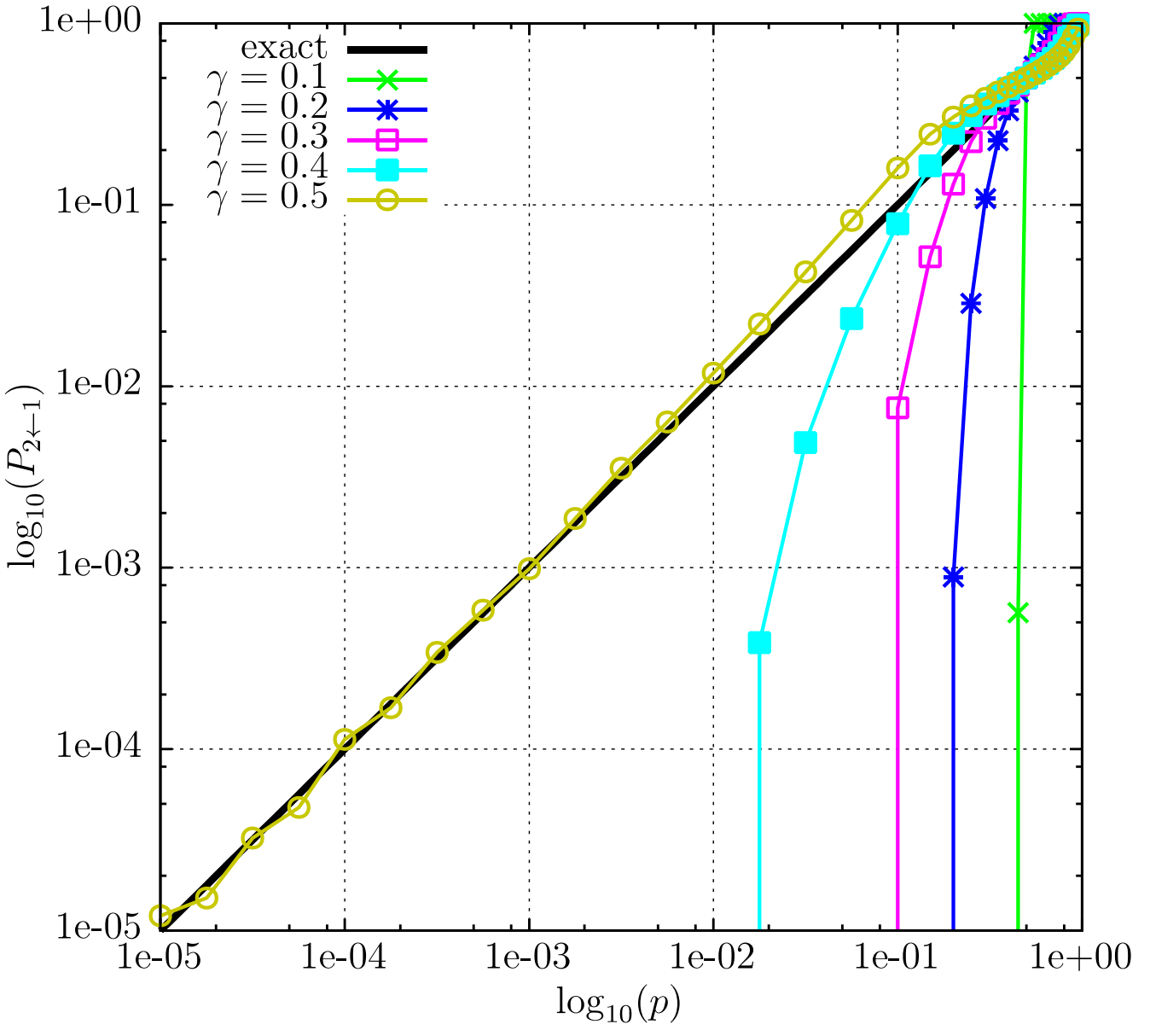
and

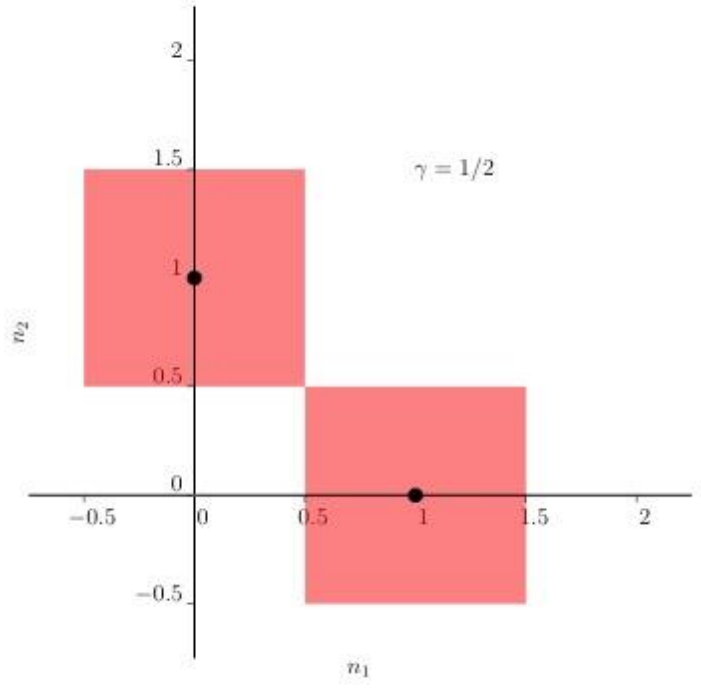
$$n_2(\infty) = p\, n_1(0) + (1-p)\, n_2(0) + 2\sqrt{p\,(1-p)}\sqrt{n_1(0)\, n_2(0)} \cdot \sin\left(q_2(0) - q_1(0) + \frac{\beta - \alpha}{2} \right)$$

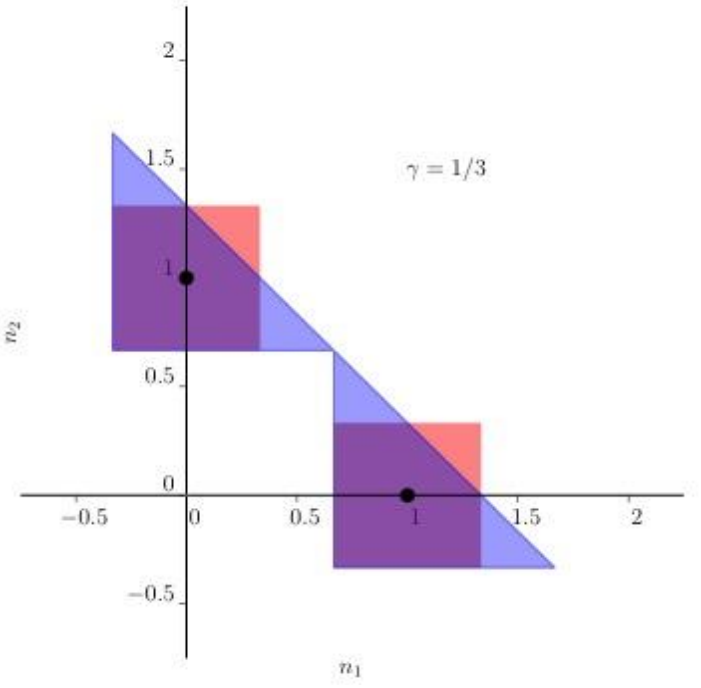
If all $n_k \to n_k + \gamma$, then the only change is that

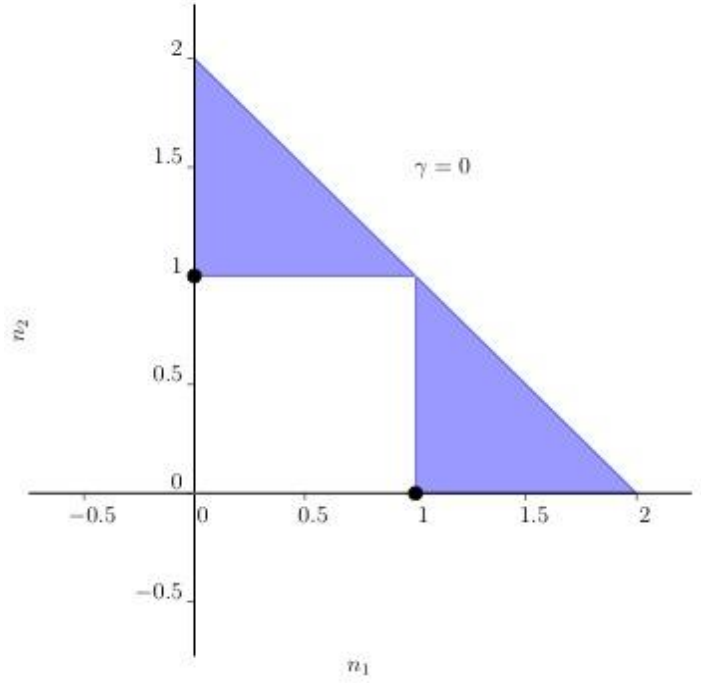
$$\sqrt{n_1(0)\, n_2(0)} \to \sqrt{(n_1 + \gamma)\,(n_2(0) + \gamma)}$$

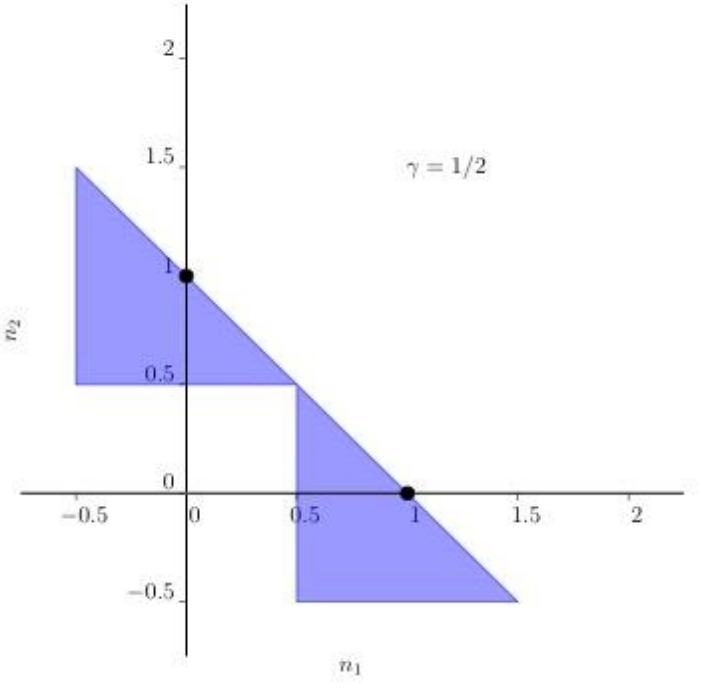

exact
$\gamma = 0.1$
$\gamma = 0.2$
$\gamma = 0.3$
$\gamma = 0.4$
$\gamma = 0.5$
$P_{2\leftarrow 1}$
p
0.0
0.1
0.2
0.3
0.4
0.5


exact
$\gamma = 0.1$
$\gamma = 0.2$
$\gamma = 0.3$
$\gamma = 0.4$
$\gamma = 0.5$
1e+00
1e-01
1e-02
1e-03
1e-04
1e-05
1e-05
1e-04
1e-03
1e-02
1e-01
1e+00
$\log_{10}(P_{2\leftarrow 1})$
$\log_{10}(p)$

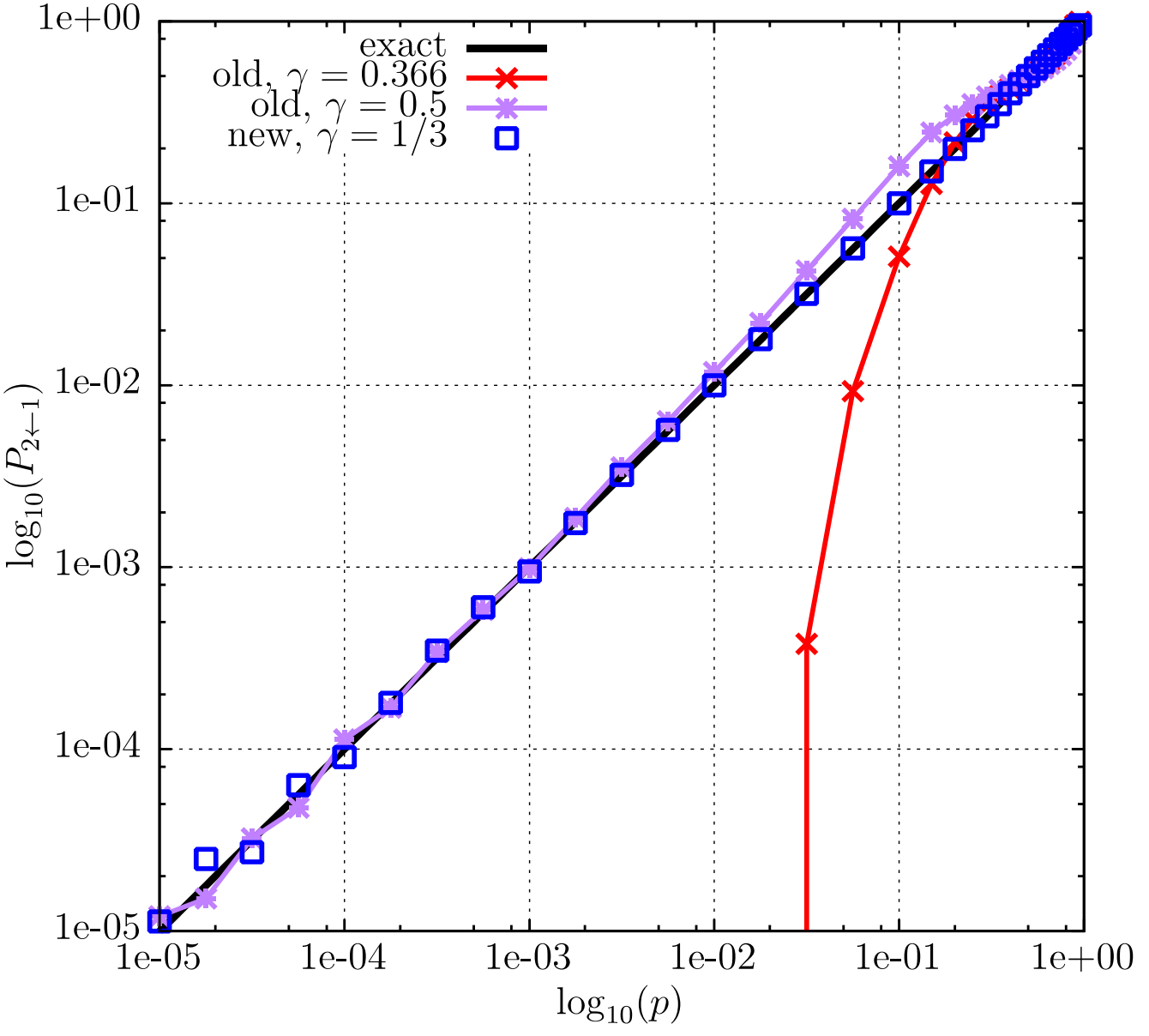


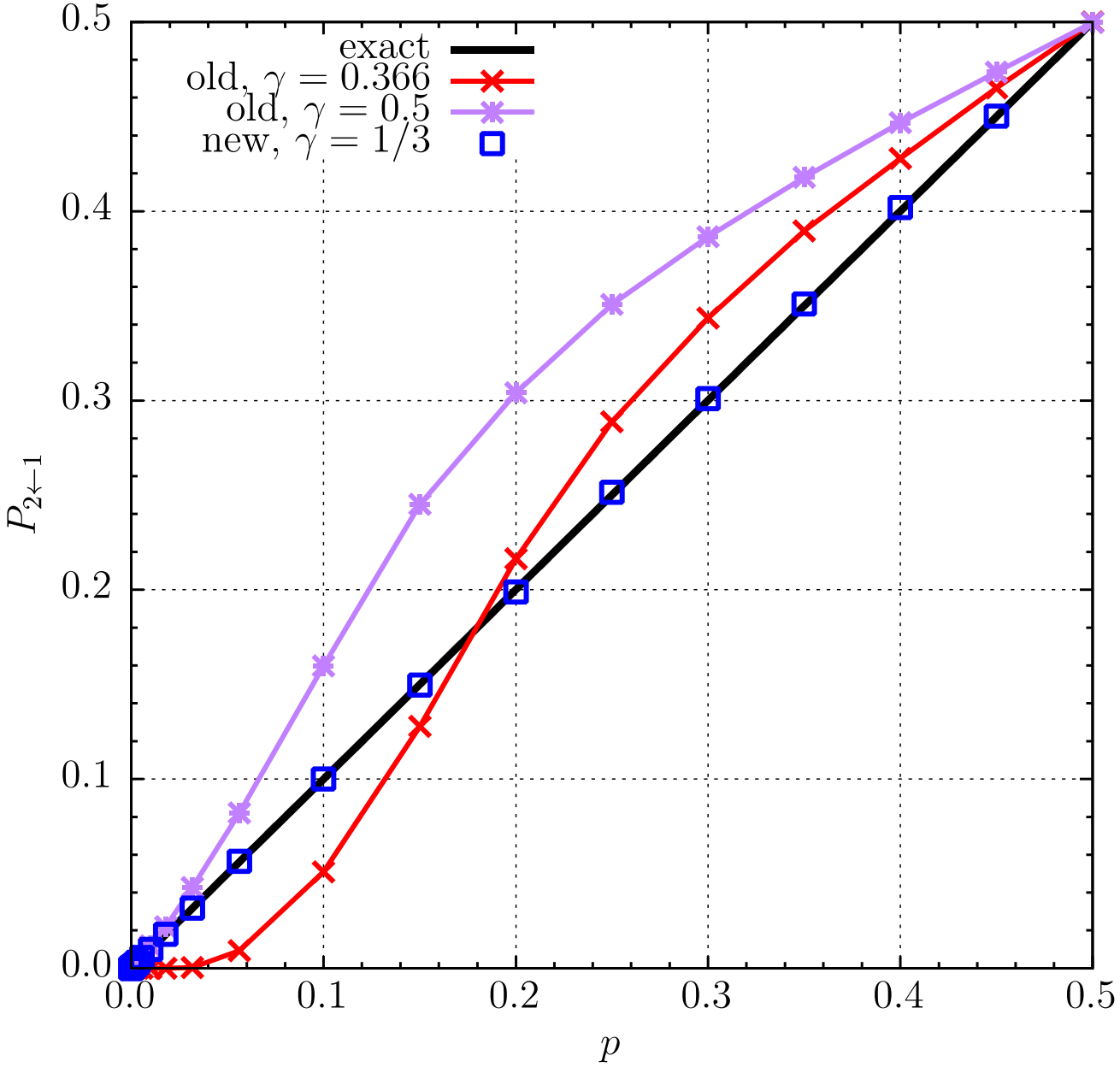


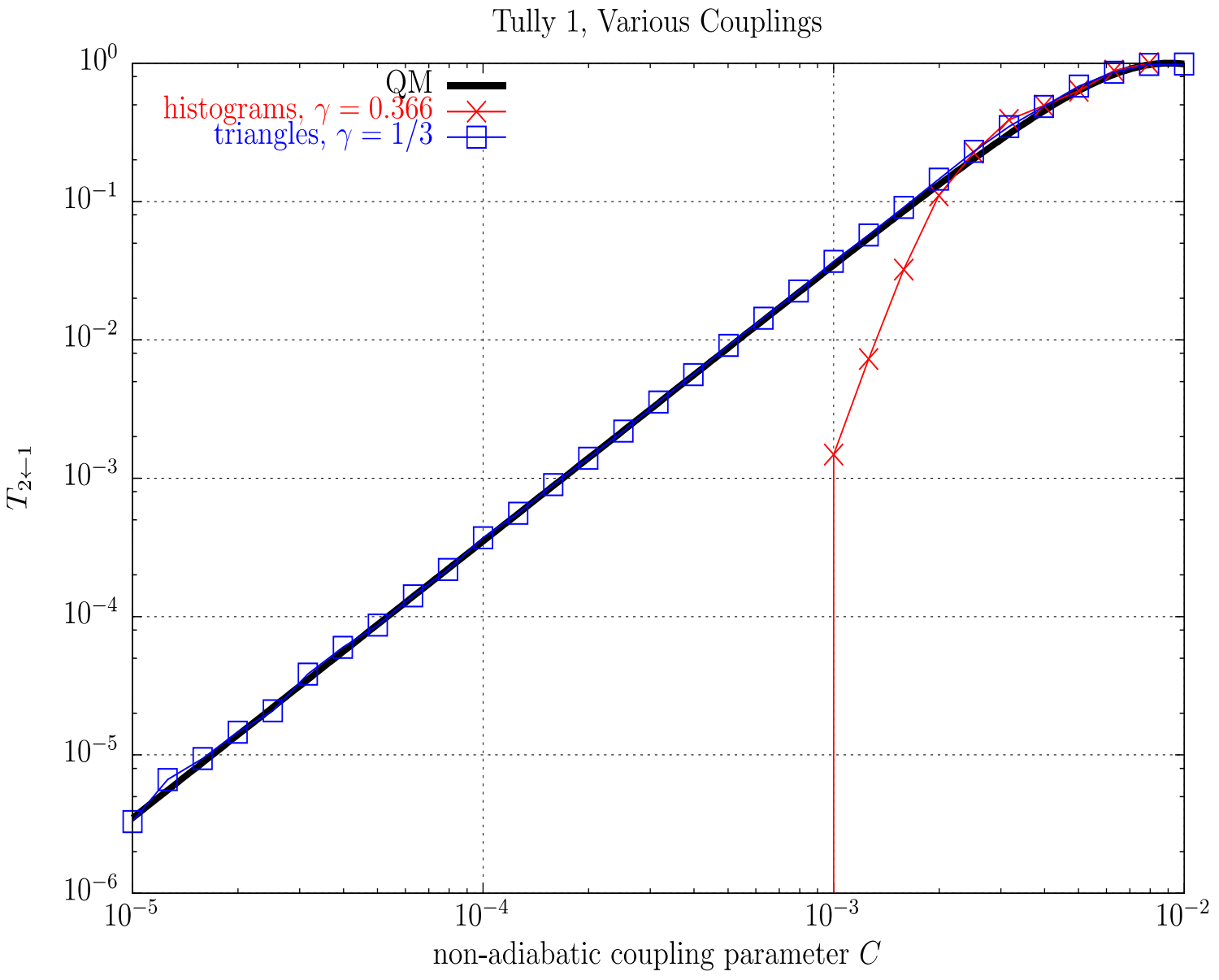




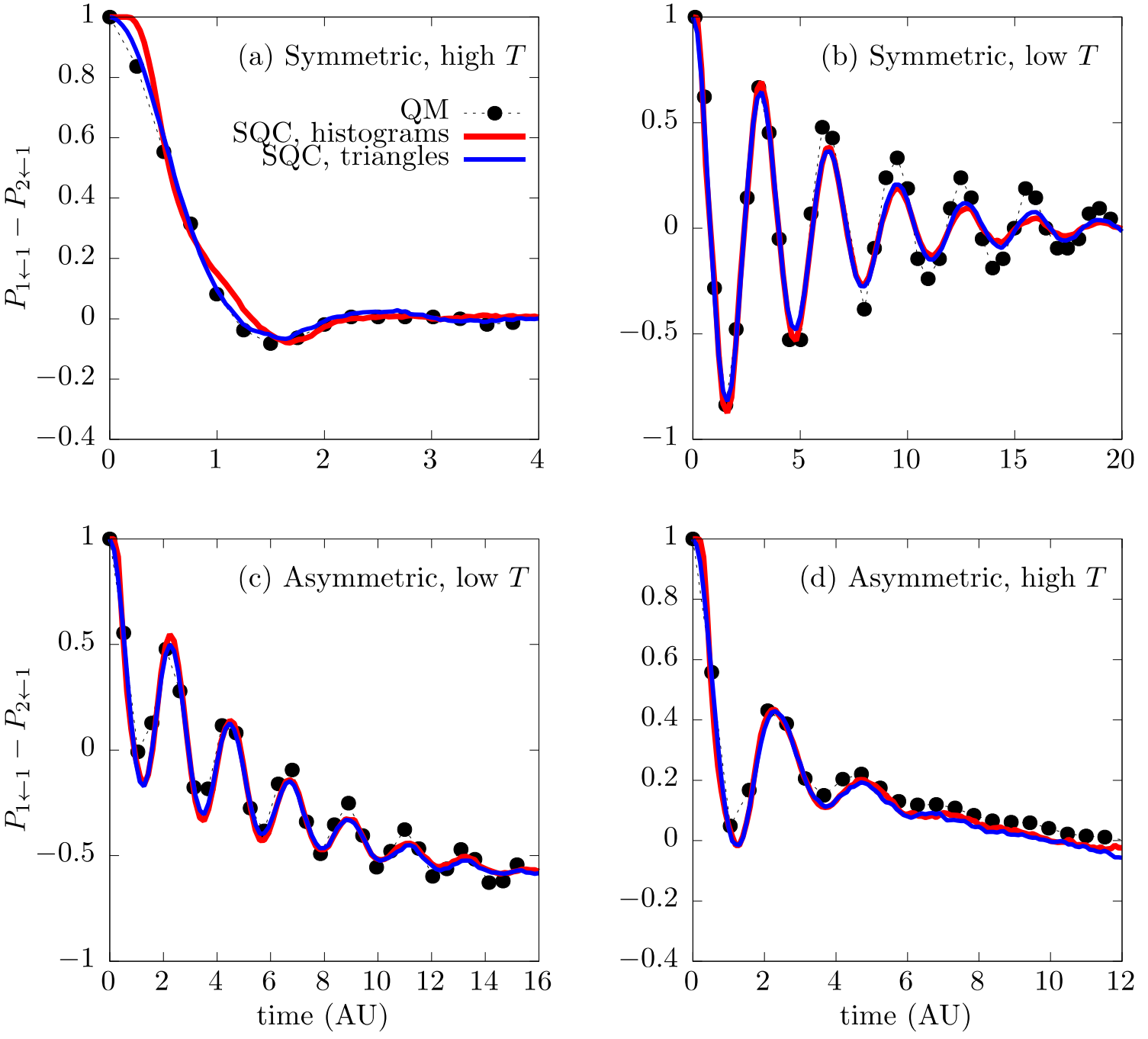
γ = 1/3 puts the integer actions (1,0) and (0,1) at the centroids of the triangles


exact
old, $\gamma = 0.366$
old, $\gamma = 0.5$
new, $\gamma = 1/3$
1e+00
1e-01
1e-02
1e-03
1e-04
1e-05
$\log_{10}(P_{2\leftarrow 1})$
1e-05
1e-04
1e-03
1e-02
1e-01
1e+00
$\log_{10}(p)$


exact
old, $\gamma = 0.366$
old, $\gamma = 0.5$
new, $\gamma = 1/3$
$P_{2\leftarrow 1}$
p
0.0
0.1
0.2
0.3
0.4
0.5


Tully 1, Various Couplings
QM
histograms, $\gamma = 0.366$
triangles, $\gamma = 1/3$
$T_{2\leftarrow 1}$
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
non-adiabatic coupling parameter C

Validation on Previous Spin-Boson Benchmarks



Same 4 Versions (as above)

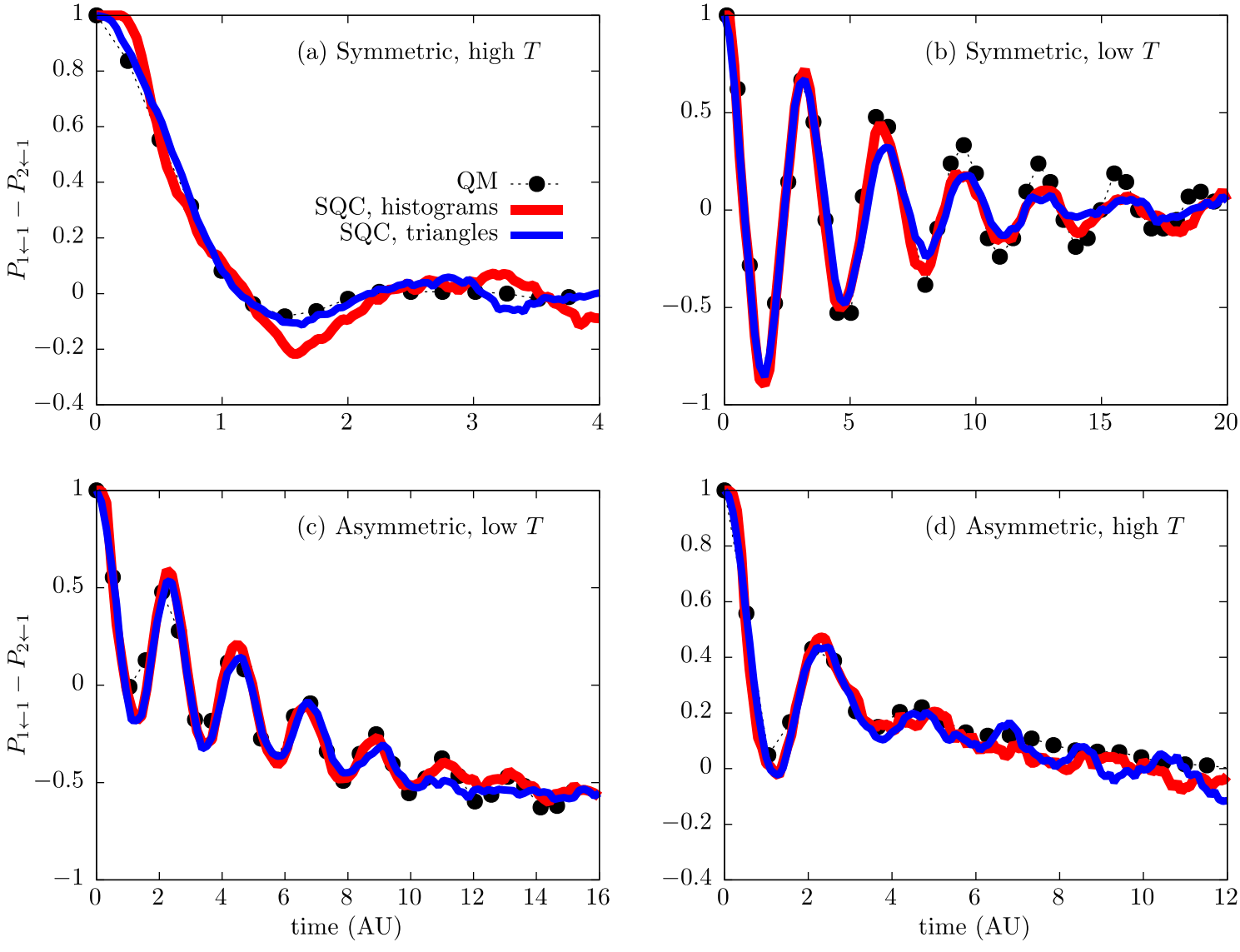
Symmetric (ϵ=*0*) at High Temp: $\beta\Delta$=*0.1*, α=*0.09*, $\omega_c\Delta$=*2.5*

Symmetric (ϵ=*0*) at Low Temp: $\beta\Delta$=*5*, α=*0.09*, $\omega_c\Delta$=*2.5*

Asymmetric (ϵ=*1*) at Low Temp: $\beta\Delta$=*5*, α=*0.1*, $\omega_c\Delta$=*2.5*

Asymmetric (ϵ=*1*) at High Temp: $\beta\Delta$=*0.25*, α=*0.1*, $\omega_c\Delta$=*1*

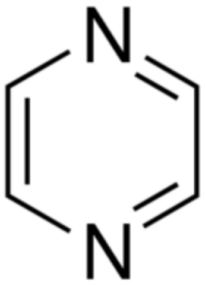
Same Calculations with Only 1000 Trajectories

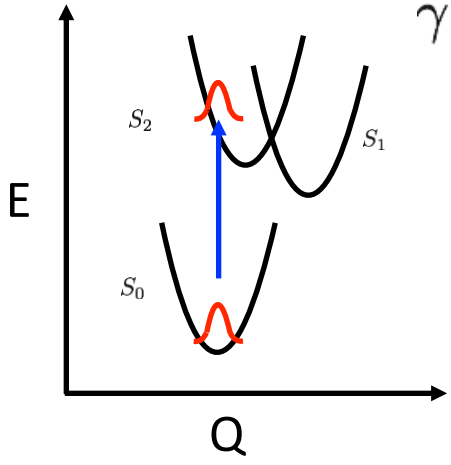


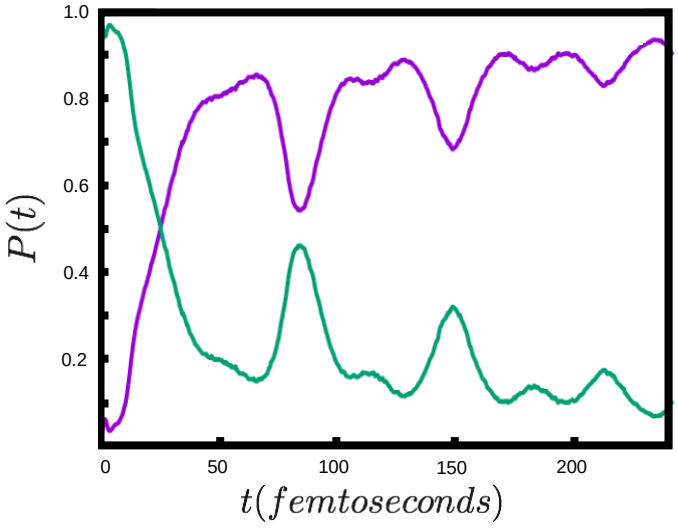
SQC: PYRAZINE

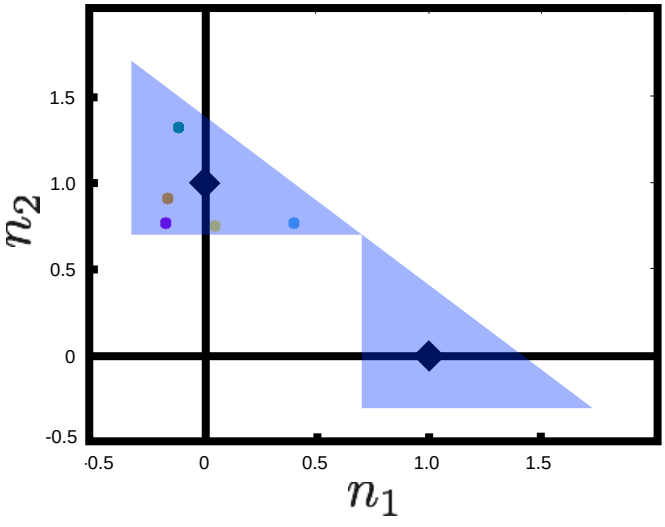
$\gamma = \frac{1}{3}$

no unique pre-limit delta function!





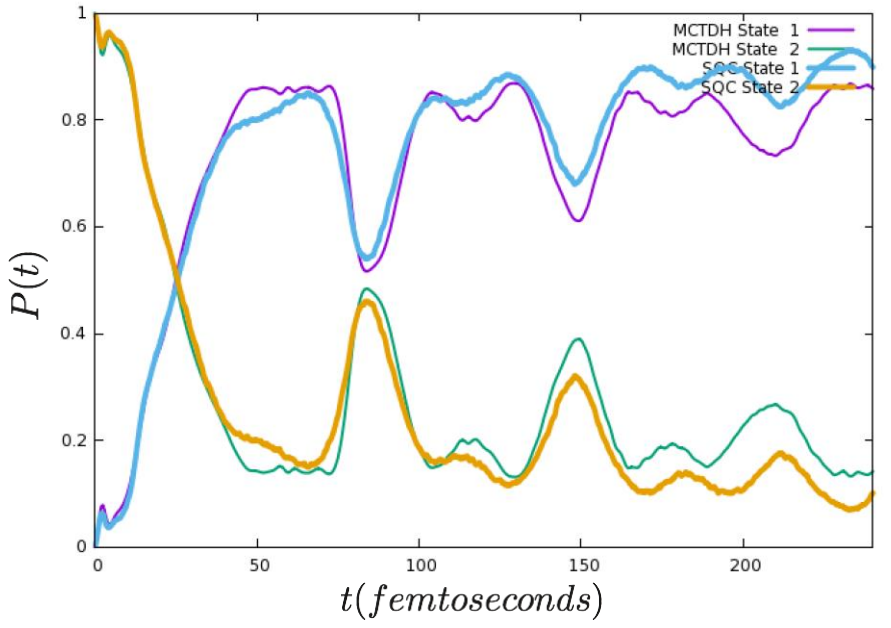




A. Raab, G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **110**, 936 (1999)

SQC: PYRAZINE

SQC vs *exact* MCTDH calculation



Wigner Functions in Action-Angle Variables

Standard Wigner function corresponding to operator $\hat{A}$ (with $\hbar = 1$),

$$W(p,x) = \int d\Delta x \; e^{-ip\Delta x} \left\langle x + \tfrac{\Delta x}{2} \right| \hat{A} \left| x - \tfrac{\Delta x}{2} \right\rangle \tag{1}$$

For the density (matrix) operator

$$\hat{A}_{N,N'} = |N\rangle \langle N'| \tag{2}$$

for a set of discrete states $\{|N\rangle\}, N = 0, 1, \ldots,$ the corresponding Wigner functions are

$$W_{N,N'}(p,x) = \int d\Delta x \; e^{-ip\Delta x} \left\langle x + \tfrac{\Delta x}{2} \middle| N \right\rangle \left\langle N' \middle| x - \tfrac{\Delta x}{2} \right\rangle \tag{3}$$

For the two lowest states of a harmonic oscillator the Wigner function for the 2×2 density matrix is

$$\begin{aligned} W_{0,0}(p,x) &= \int d\Delta x \; e^{-ip\Delta x} \left\langle x + \tfrac{\Delta x}{2} \middle| 0 \right\rangle \left\langle 0 \middle| x - \tfrac{\Delta x}{2} \right\rangle \\ &= 2\, e^{-(p^2+x^2)} \end{aligned} \tag{4a}$$

$$W_{1,1}(p,x) = 4(p^2 + x^2 - \tfrac{1}{2})\, e^{-(p^2+x^2)} \tag{4b}$$

$$W_{0,1}(p,x) = W^*_{1,0}(p,x) = 2\sqrt{2}\,(x + ip)\, e^{-(p^2+x^2)}, \tag{4c}$$

where dimensionless variables have been used for which $\hbar = \omega = m = 1$. Replacing (p,x) by action-angle variables (n,q),

$$\begin{aligned} x(n,q) &= \sqrt{2n}\, \cos(q) \\ p(n,q) &= -\sqrt{2n}\, \sin(q) \end{aligned} \tag{5}$$

gives the density matrix Wigner functions of Eq. (4) in terms of (n,q)

$$W_{0,0}(n,q) = 2\, e^{-2n} \tag{6a}$$

$$W_{1,1}(n,q) = 4\,(2n - \tfrac{1}{2})\, e^{-2n} \tag{6b}$$

$$W_{1,0}(n,q) = W^*_{0,1}(n,q) = 4\sqrt{n}\, e^{-2n}\, e^{iq}. \tag{6c}$$

But another way: carry out the Wigner transformation directly in a-a variables,

$$W_{N,N'}(n,q) = \int d\Delta q\, e^{-in\Delta q} \left\langle q + \tfrac{\Delta q}{2} \middle| N \right\rangle \left\langle N' \middle| q - \tfrac{\Delta q}{2} \right\rangle \tag{7}$$

where the bra-ket $\langle q|N\rangle$ (i.e., the "wavefunction" in angle space for the "state" $|N\rangle$) is

$$\langle q|N\rangle = \frac{e^{iNq}}{\sqrt{2\pi}}. \tag{8}$$

A simple calculation gives

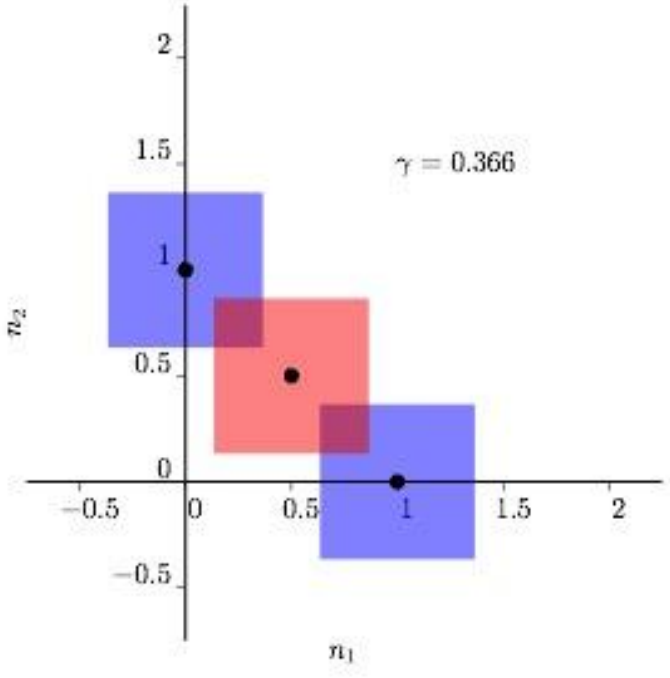
$$W_{N,N'}(n,q) = e^{i(N-N')q}\, \delta(n - \tfrac{N+N'}{2}) \tag{9a}$$

E.g., for diagonal elements ($N' = N$),

$$W_{N,N}(n,q) = \delta(n - N) \tag{9b}$$

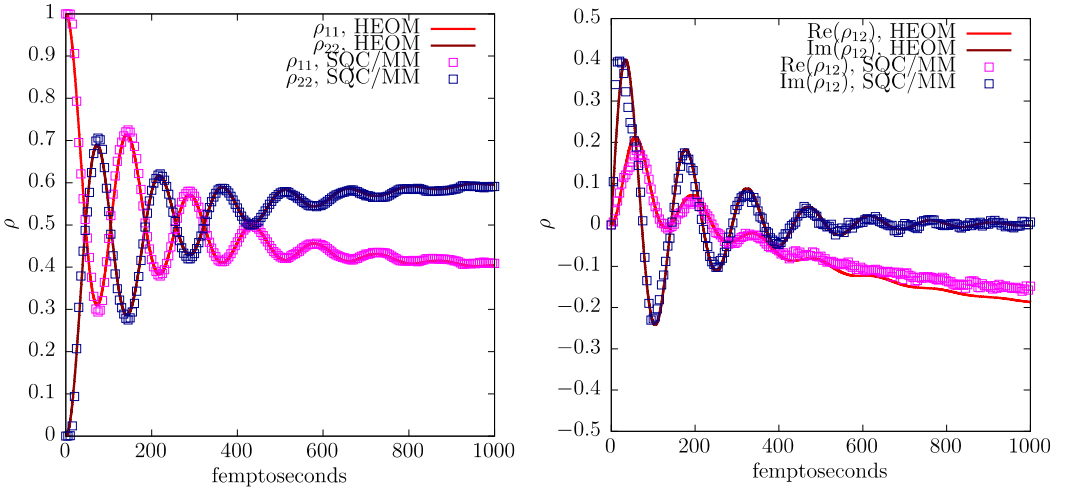
i.e., Bohr-Sommerfeld quantization

FIG. 1. SQC windowing functions for the diagonal and off-diagonal elements of the density matrix applied to a system of 2 electronic states.



Preliminary result for Ishizaki and Fleming's "site-exciton" model for light-harvesting complexes: full 2×2 SQC/MM time-dependent electronic density matrix versus benchmark results calculated using equations of motion (HEOM)

FIG. 2. SQC/MM computed density matrix $\{\rho_{ij}(t)\}$ versus HEOM results for 2-state site-exciton model (difference in site energies $\epsilon_1 - \epsilon_2 = 100$ cm^{-1}, non-adiabatic coupling $J_{12} = 100$ cm^{-1}, bath characteristic frequency $\omega_c = 53.08$ cm^{-1}, reorganization energy $\lambda = 20$ cm^{-1}, and $T = 300$ K; see Fig. 4 of Ref. 1)



REFERENCES

[1]A. Ishizaki and G. R. Fleming, The Journal of Chemical Physics **130**, 234111 (2009).

More Rigorous Derivation

$$\hat{H} = \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i,j} H_{ij}(\hat{\mathbf{R}})\ \hat{a}_i^\dagger \hat{a}_j$$

Where $\hat{a}_i^\dagger,\ \hat{a}_i$ are the creation and annihilation operators for populating electronic state *i*.

Choosing harmonic oscillators for the underlying DOF, one can express the creation/annihilation operators in terms of Cartesian variables:

$$\hat{a}_i = \frac{\hat{x}_i + i\hat{p}_i}{\sqrt{2}} \quad \hat{a}_i^\dagger = \frac{\hat{x}_i - i\hat{p}_i}{\sqrt{2}} \quad (m = \omega = \hbar = 1)$$

Then:

$$\hat{H} = \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i,j} H_{ij}(\hat{\mathbf{R}})\ \tfrac{1}{2}\left(\hat{p}_i\hat{p}_j + \hat{x}_i\hat{x}_j - \delta_{ij}\right)$$

$$= \frac{|\hat{\mathbf{P}}|^2}{2\mu} + \sum_{i} H_{ii}(\hat{\mathbf{R}})\ \tfrac{1}{2}\left(\hat{p}_i^2 + \hat{x}_i^2 - 1\right)$$

$$+ \sum_{i<j} H_{ij}(\hat{\mathbf{R}})\ \left(\hat{p}_i\hat{p}_j + \hat{x}_i\hat{x}_j\right)$$

Spin Mapping Model

Representing: $\hat{a}_i, \hat{a}_i^\dagger \rightarrow S_{x,i} \mp S_{y,i}$ for spin $\frac{1}{2}$

Classically, $S_i^\pm = \sqrt{S^2 - m_i^2}\, e^{\pm i q_i}$, $S_{i,z} = m_i$,

and with $n_i \equiv m_i + \frac{1}{2}$ (with QM values $n_i = 0$ or 1),

The classical vibronic Hamiltonian is

$$H(\mathbf{P},\mathbf{R},\mathbf{n},\mathbf{q}) = \frac{|\mathbf{P}|^2}{2\mu} + \sum_i H_{ii}(\mathbf{R})\, n_i$$

$$+ 2\sum_{i<j} H_{ij}(\mathbf{R}) \sqrt{(n_i + \gamma)(1+\gamma-n_i)} \sqrt{(n_j+\gamma)(1+\gamma-n_j)}\, \cos(q_i - q_j)$$

Extra factors are the only difference from the MM Hamiltonian

Some (ancient) History, c. 1978-79

Consider resonance effects in electronic-to-Rot/vib energy transfer [JCP **68**, 4431 (1978]:

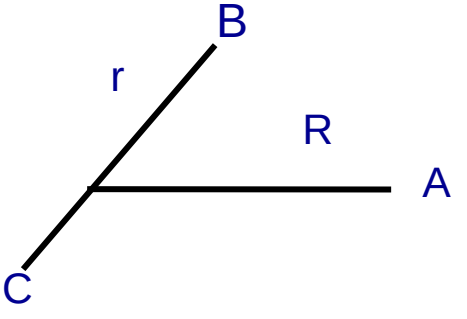
1) Does F* react with H_2?

2) Quenching of Br* by H_2: $Br*+H_2 \rightarrow Br+H_2^{\ddagger}$

$\Delta E_{Br} = 3685 \ \ cm^{-1}$

Cf. classical nuclear motion on B.O. PES's

$W_n(r,R)$



$W_n(t) = W_n(r(t),R(t))$ $\qquad$ $r(t) \sim \cos(\omega t)$

A classical model for electronic degrees of freedom (i.e., N electronic states)

cf. McCurdy, Meyer, Miller JCP 1978-79

- Need to treat nuclear and electronically dof on **equal footing** to have **dynamically consistent** description.
- \ If one treats nuclei classically, one needs to treat electronic dof also clasically [cf. **resonance E-V,R transfer** in $F^* + H_2(j=0)$

$$\rightarrow \; F + H_2(j=2), Br^* + H_2(v=0) \rightarrow Br + H_2(v=1)$$

Original Approach (Miller & McCurdy JCP 1978)

- 2 level system ᵕ spin $\frac{1}{2}$ system

- Most general spin $\frac{1}{2}$ Hamiltonian

$$\hat{H} = a + a_x \hat{S}_x + a_y \hat{S}_y + a_z \hat{S}_z$$

- Classically, $S_z \to m$

$$S_y \to \sqrt{S^2 - m^2}\,\sin q$$

$$S_x \to \sqrt{S^2 - m^2}\,\cos q$$

$$n \circ\ m + \tfrac{1}{2}(= 0\ or\ 1),\ S^2 = \tfrac{1}{2}(\tfrac{1}{2}+1) = \tfrac{3}{4}$$

$$or\ (\tfrac{1}{2}+\tfrac{1}{2})^2 = 1$$

P

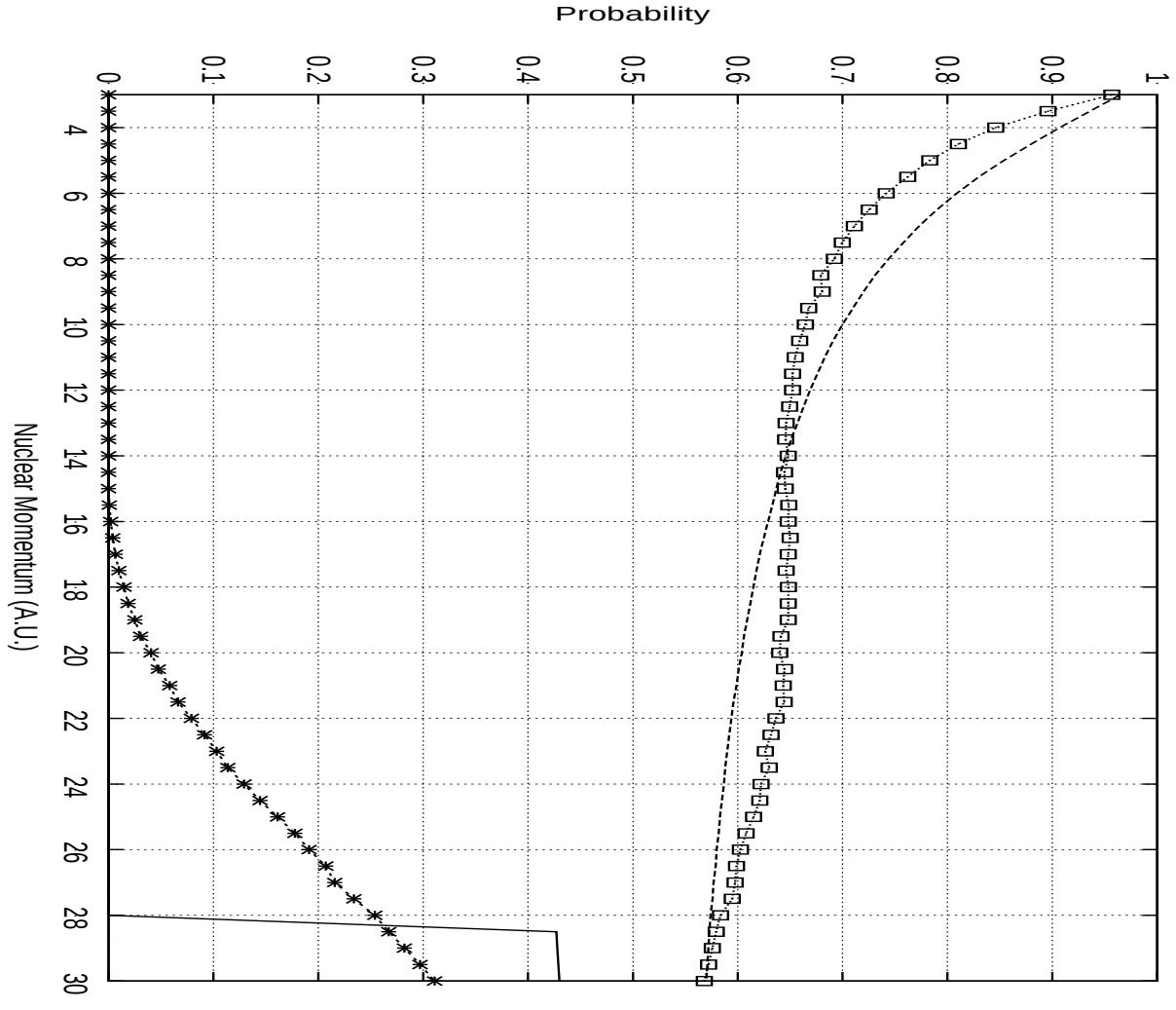
$$H_{e\ell}(n,q) = nH_{11} + (1-n)H_{00} + \sqrt{n - n^2 + l}\ (H_{10}e^{iq} + H_{01}e^{-iq})$$

$$l = S^2 - \tfrac{1}{4}\ (= \tfrac{1}{2}\text{or}\tfrac{3}{4})$$

$$\setminus\ H(\mathbf{P},\mathbf{R},n,q) = \frac{\mathbf{P}^2}{2m} + H_{el}(n,q;\mathbf{R})$$

$$H_{ij} = H_{ij}(\mathbf{R})$$

Tully #3


Probability
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Nuclear Momentum (A.U.)
4
6
8
10
12
14
16
18
20
22
24
26
28
30