

The Path Integral Formulation of Quantum and Statistical Mechanics

Nancy Makri

*Departments of Chemistry and Physics
University of Illinois at Urbana-Champaign*

II. Numerical Methodology and Applications

Quantum dissipative systems

System – harmonic bath models

$$H = \underbrace{\frac{p_s^2}{2m_0} + V_0(s)}_{\text{system}} + \sum_j \left(\underbrace{\frac{p_j^2}{2m_j}}_{\text{bath}} + \frac{1}{2} m_j \omega_j^2 q_j^2 - \underbrace{c_j s q_j}_{\text{coupling}} \right)$$

Classically, the system satisfies the generalized Langevin equation:

$$m_0 \ddot{s}(t) + \int_0^t \eta(t-t') \dot{s}(t') + V_0'(s(t)) = \xi(t)$$

Quantum dynamics: non-interacting blip approximation (Leggett and coworkers)

Systems in contact with nonlinear condensed phase environments

$$H = H_0(s, p_s) + H_b(\mathbf{q}, \mathbf{p}, s)$$

PATH INTEGRAL METHODOLOGY

Path integral – influence functional formalism

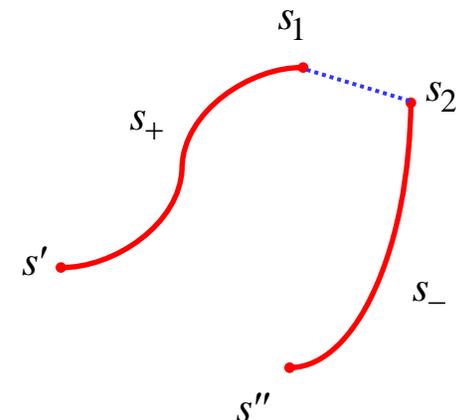
$$H = H_0(s, p_s) + H_b(\mathbf{q}, \mathbf{p}, s)$$

s : observable system
 \mathbf{q} : multidimensional bath

$$\begin{aligned}\tilde{\rho}(s', s''; t) &= \sum_{\text{system paths } s_{\pm}} \sum_{\text{bath paths } \mathbf{q}_{\pm}} K_0[s_{\pm}] K_b[s_{\pm}, \mathbf{q}_{\pm}] \rho_0(s_1, s_2, \mathbf{q}_1, \mathbf{q}_2) \\ &= \sum_{\text{system paths } s_{\pm}} K_0[s_{\pm}] \tilde{\rho}_0(s_1, s_2) F[s_{\pm}]\end{aligned}$$

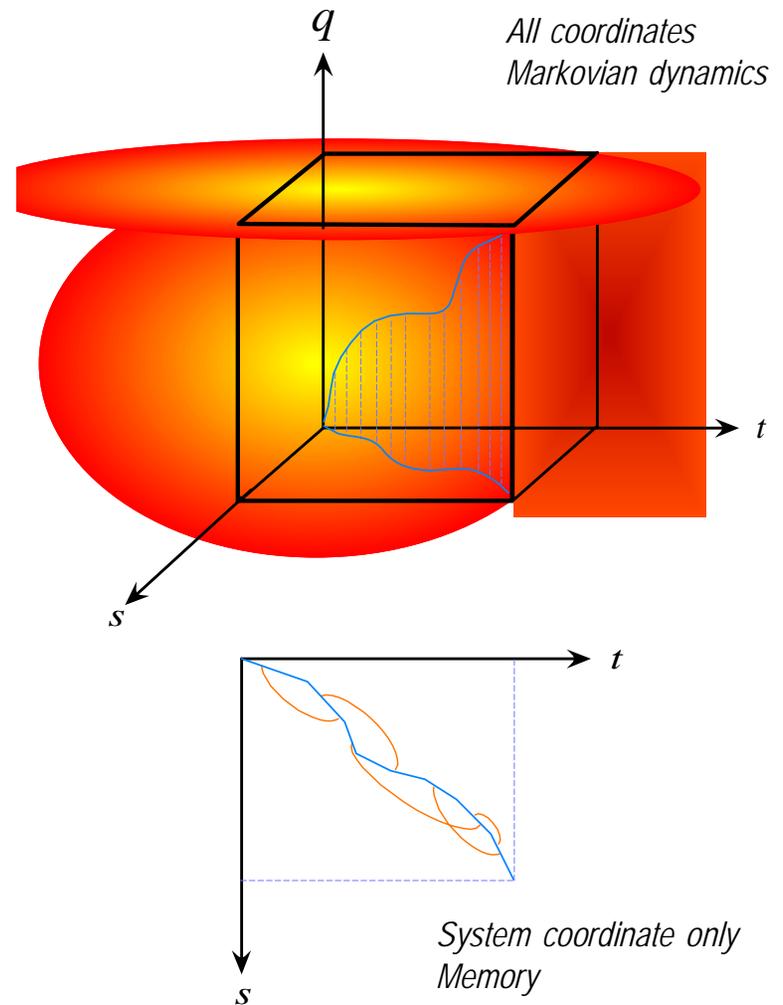
F : influence functional

- Choose a time step, split the time evolution operators and discretize the paths.
- In general, the influence functional requires a many-body calculation in itself.
- The sum over system paths is tractable only for short time.



$$\tilde{\rho}(s', s''; t) = \sum_{\text{system paths } s_{\pm}} K_0[s_{\pm}] \tilde{\rho}_0(s_1, s_2) F[s_{\pm}]$$

- The number of paths grows *exponentially* with the number of time steps.
- The influence functional introduces *nonlocal couplings* analogous to memory effects in GLE.
- The reduced-dimension path integral is *not* equivalent to a one-dimensional Schrodinger equation.
- Markovian (memory-free) evolution is recovered only in the infinite temperature limit [Leggett *et al.*]



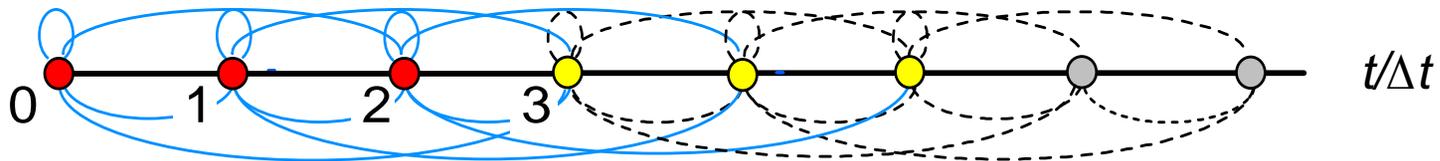
Influence functional from a *harmonic* bath

$$F[s_{\pm}] = \exp \left\{ - \int_0^t dt' \int_0^{t'} dt'' (s_+(t') - s_-(t')) \left(\alpha(t' - t'') s_+(t'') - \alpha^*(t' - t'') s_-(t'') \right) \right\}$$

In discrete form,

$$F(s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm}) = \exp \left\{ - \sum_{k_1=0}^N \sum_{k_2=0}^N \left(\left(s_{k_1}^+ - s_{k_1}^- \right) \left(\eta_{k_1 k_2} s_{k_2}^+ - \eta_{k_1 k_2} s_{k_2}^- \right) \right) \right\}$$

- The coefficients are given by the force autocorrelation function of the bath.
- The force autocorrelation function of the dissipative bath decays with time. This behavior is a consequence of *decoherence*.
- The nonlocal interactions drop off rapidly if the bath has a broad spectrum, thus the nonlocality has a finite span.
- Discarding negligible interactions the remaining terms leads to a structure that can be exploited to evaluate the path integral by an iterative procedure.

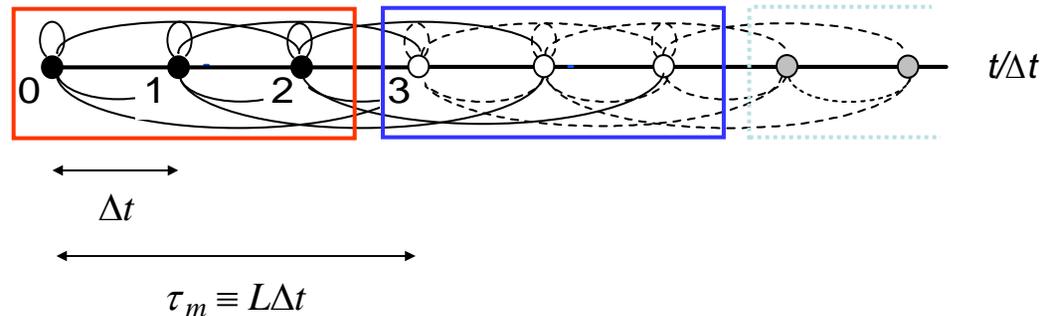


Iterative propagation for a system coupled to a harmonic bath

$$\mathbf{R}(kL + L) = \mathbf{T} \cdot \mathbf{R}(kL)$$

R: vector (functional) of (statistically significant) path segments of length $L\Delta t$.

T: propagator matrix connecting adjacent path segments.



Only path segments that span the memory length are stored. If M such path segments are used, the result after N iterations is equivalent to that which would have been obtained by including explicitly M^N paths.

e.g. $M \sim 10^4$, $N = 1000 \Rightarrow 10^{4000}$ paths included

- D. E. Makarov and N. Makri, *Chem. Phys. Lett.* **221**, 482 (1994).
- N. Makri and D. E. Makarov, *J. Chem. Phys.* **102**, 4600, 4611 (1995).
- E. Sim and N. Makri, *Chem. Phys. Lett.* **249**, 224 (1996).
- E. Sim and N. Makri, *Comp. Phys. Commun.* **99**, 335 (1997).
- N. Makri, *J. Phys. Chem.* **102**, 4414 (1998).

Properties

- **Stability**

If all paths are included in the propagator functional, the trace of the reduced density matrix is conserved for arbitrary time periods.

- **Thermodynamic limit**

With nonzero dissipation, the propagator matrix χ has a stable fixed point. The corresponding eigenvalue yields the equilibrium density matrix.

- **Rates without explicit propagation**

The smallest real nonzero eigenvalue of the propagator matrix gives the relaxation rate coefficient. Complex eigenvalues are associated with coherences.

The influence functional for *general nonlinear environments* can be expressed in terms of a cumulant expansion:

$$\begin{aligned}
 & F\left(s_0^\pm, s_1^\pm, \dots, s_N^\pm\right) \\
 &= \exp \left\{ - \sum_{k_1=0}^N \left(\alpha_{k_1}^+ s_{k_1}^+ + \alpha_{k_1}^- s_{k_1}^- \right) - \sum_{k_1=0}^N \sum_{k_2=0}^N \left(\beta_{k_1 k_2}^{++} s_{k_1}^+ s_{k_2}^+ + \beta_{k_1 k_2}^{+-} s_{k_1}^+ s_{k_2}^- + \dots \right) \right. \\
 & \quad \left. - \sum_{k_1=0}^N \sum_{k_2=0}^N \sum_{k_3=0}^N \left(\gamma_{k_1 k_2 k_3}^{+++} s_{k_1}^+ s_{k_2}^+ s_{k_3}^+ + \gamma_{k_1 k_2 k_3}^{++-} s_{k_1}^+ s_{k_2}^+ s_{k_3}^- + \dots \right) - \dots \right\}
 \end{aligned}$$

It can be shown that the various coefficients are given by *multi-time* correlation functions of the bath.

- N. Makri, *J. Phys. Chem.* **103**, 2823 (1999).

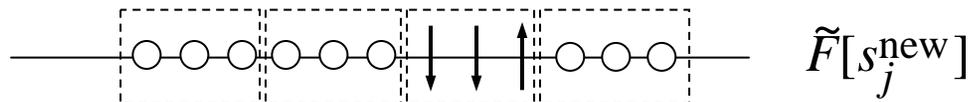
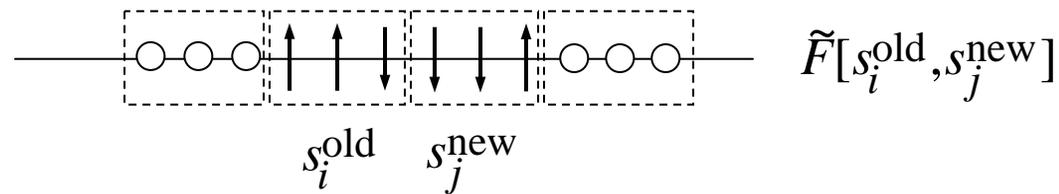
- ❑ In macroscopic environments there is extensive dephasing and the correlation functions decay. This fact restricts the extent of nonlocality.
- ❑ The finite range of nonlocal interactions can be exploited to evaluate the path integral via an iterative procedure.

Iterative algorithm for an arbitrary bath

- Construct an array \mathbf{R} of (statistically significant) path segments whose length equals the memory span $L\Delta t$.
- Propagate \mathbf{R} by one memory length by multiplying with a propagator matrix \mathbf{T} .

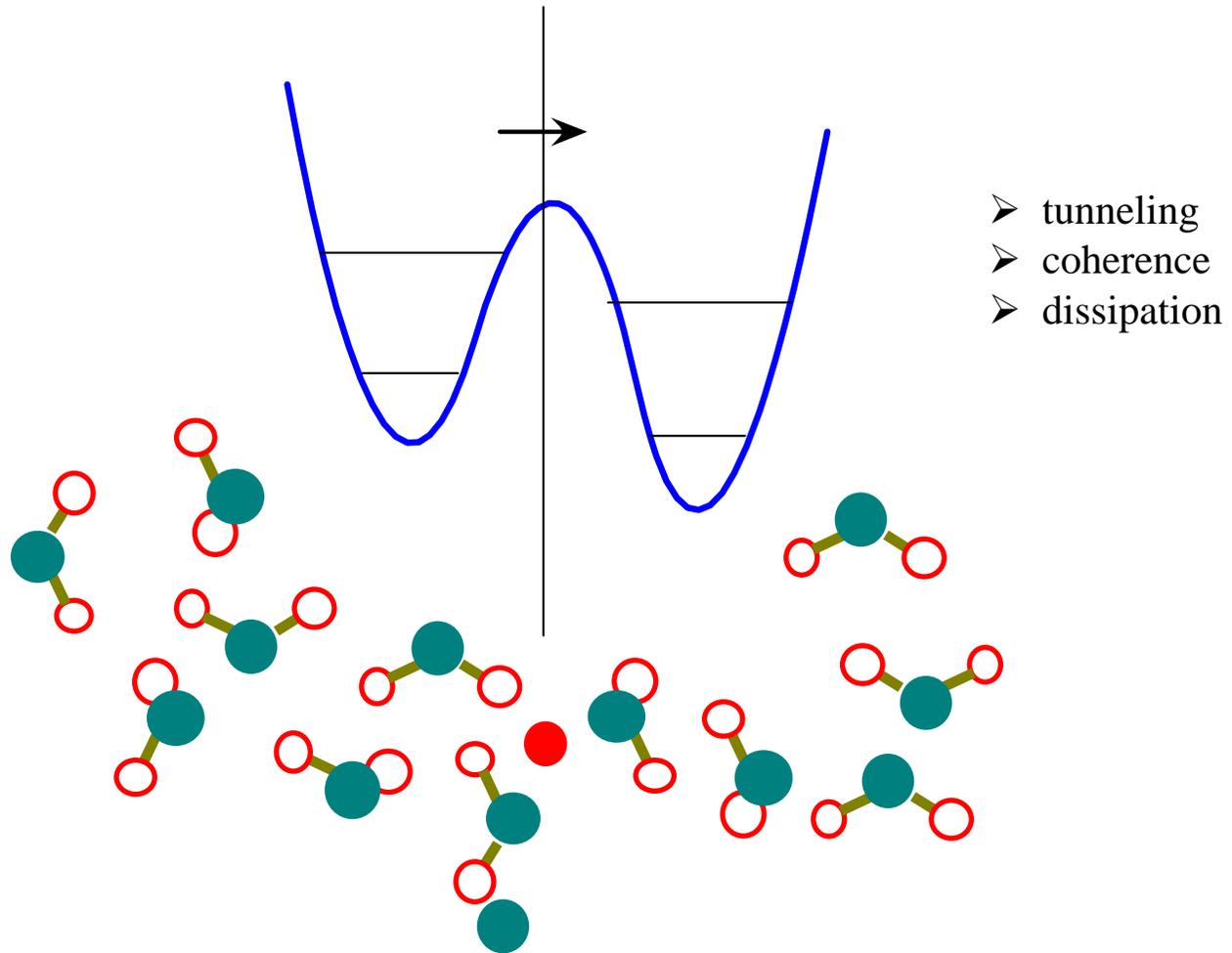
$$\mathbf{R}(kL + L) = \mathbf{T} \cdot \mathbf{R}(kL)$$

$$T_{ij}[s_i^{\text{old}}, s_j^{\text{new}}] = K_0[s_i^{\text{old}}, s_j^{\text{new}}] \frac{\tilde{F}[s_i^{\text{old}}, s_j^{\text{new}}]}{\tilde{F}[s_j^{\text{new}}]}$$



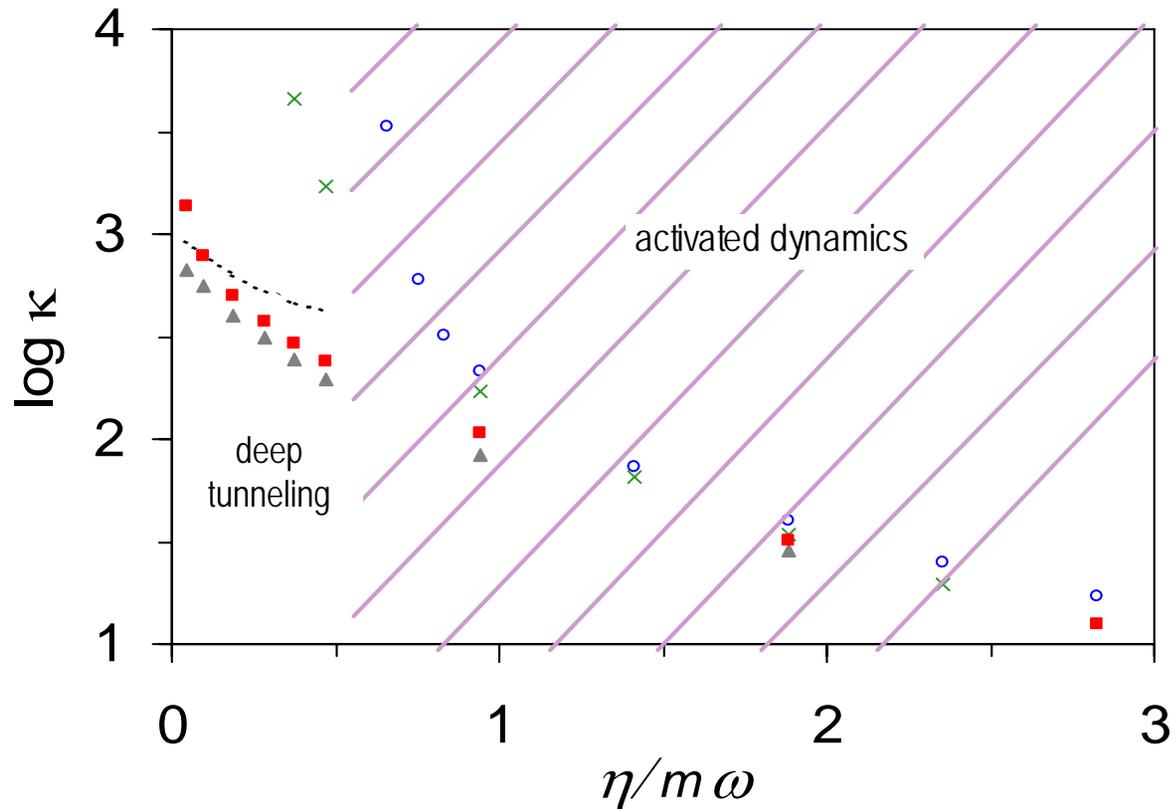
- The influence functional can be evaluated using Forward-Backward Semiclassical Dynamics (FBSD)

Reaction Rates



Quantum Transmission Coefficient

Temperature around crossover



Red squares:

Open circles:

Green crosses:

Dashed line:

Gray triangles:

Numerical path integral results

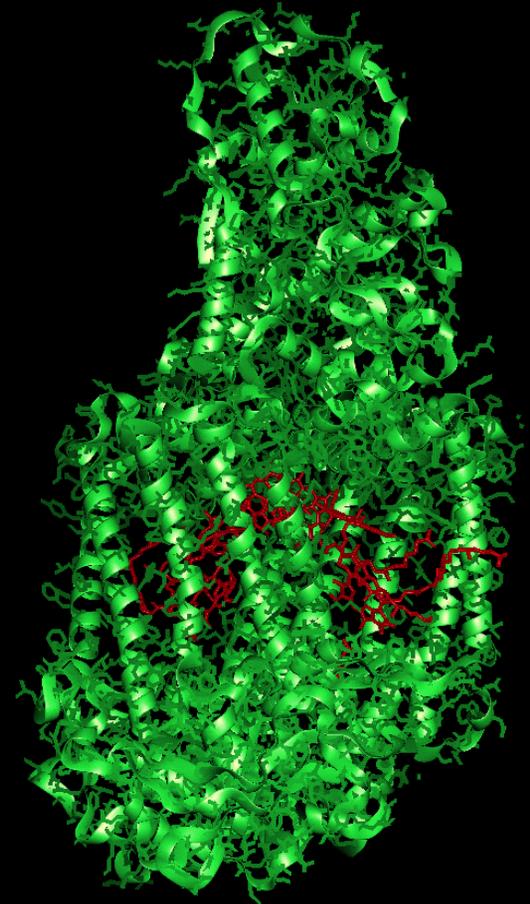
Wolynes correction factor (quantum Grote Hynes theory)

Parabolic barrier estimate of periodic orbit theory

Normal mode estimate of periodic orbit theory

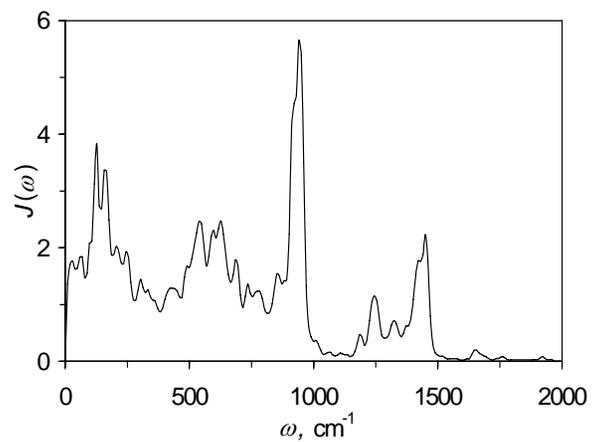
Quantum centroid density approximation

Electron transfer in photosynthesis

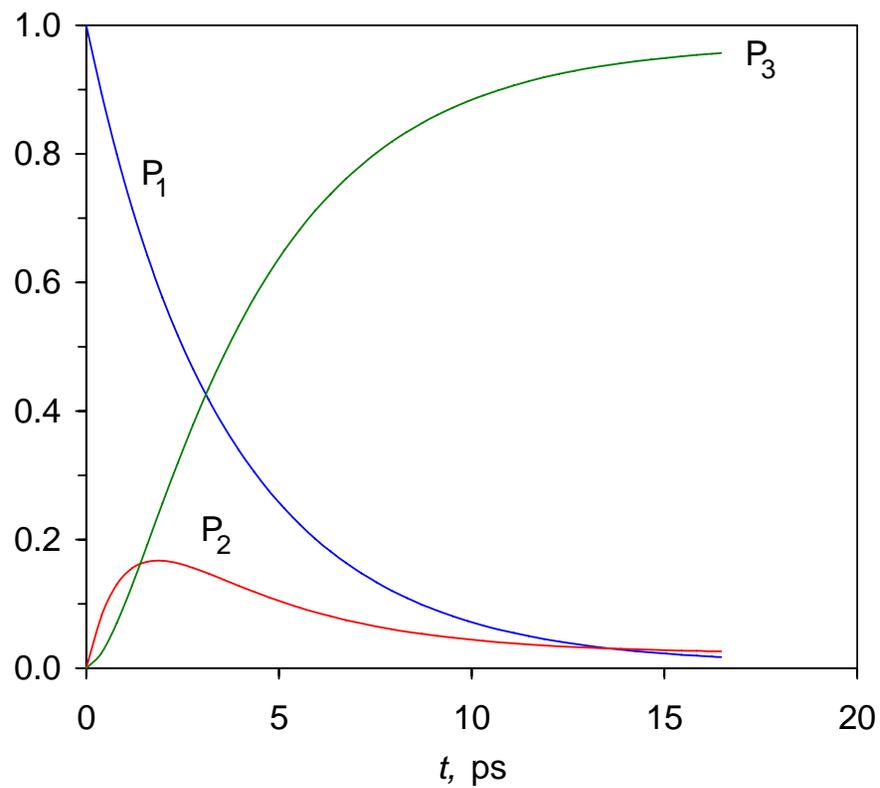


- ◆ Long-range electron transfer
- ◆ Fast process (time constant ~ 3 ps)
- ◆ High quantum yield

Spectral density from classical MD simulations (Chandler et al.)

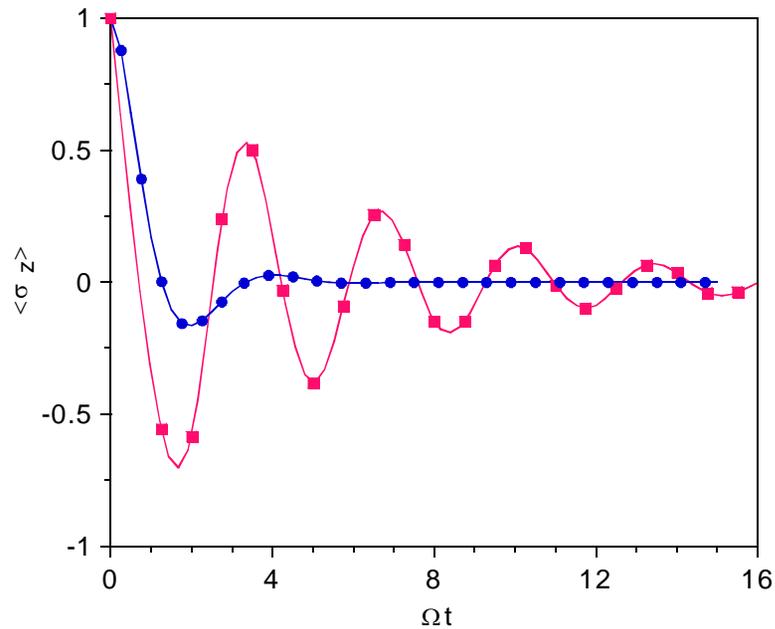


Path integral results:
Electronic populations vs. time



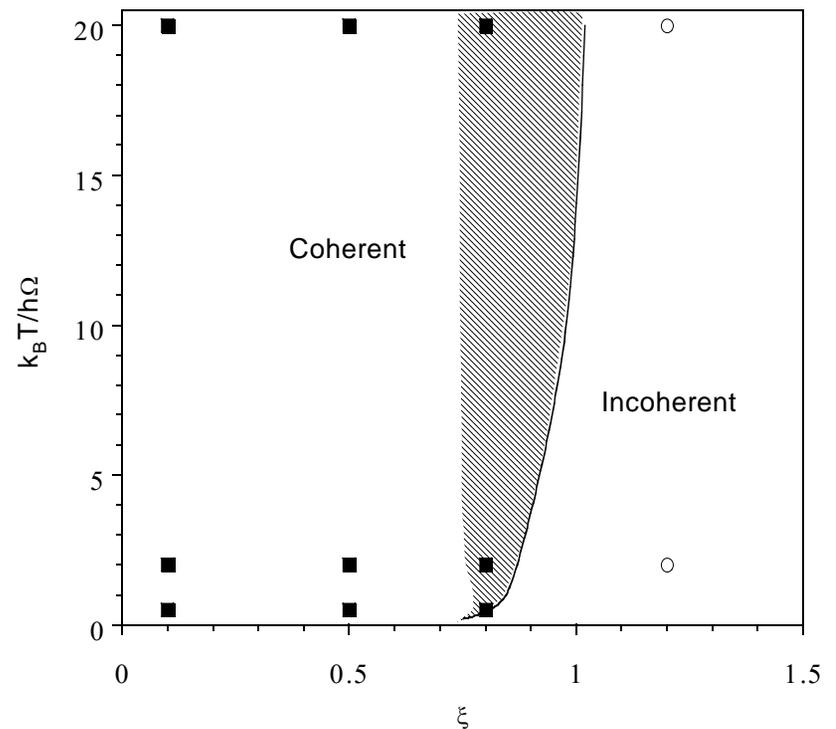
A two-level system in a bath of two-level systems

$$H = -\hbar\Omega\sigma_x^0 - \sum_{i=1}^n \frac{1}{2}\hbar\omega_i\sigma_x^i - \sigma_z^0 \sum_{i=1}^n c_i \sqrt{\frac{\hbar}{2\omega_i}}\sigma_z^i$$



— $\hbar\Omega\beta=2, \quad \xi=0.1$

— $\hbar\Omega\beta=0.05, \quad \xi=0.5$



Phase diagram

- K. Forsythe and N. Makri, *Phys. Rev. E* (July 1, 1999).

Driven dissipative two-level systems

Simplest paradigm for control of quantum dissipative dynamics

$$H = -\hbar\Omega\sigma_x + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 q_j^2 + c_j\sigma_z q_j \right) + V_0\sigma_z \cos\omega_0 t$$

In the absence of driving, the dissipative TLS exhibits

- Damped oscillations (generally, low temperature and weak friction)
- Incoherent relaxation (high temperature, strong friction)

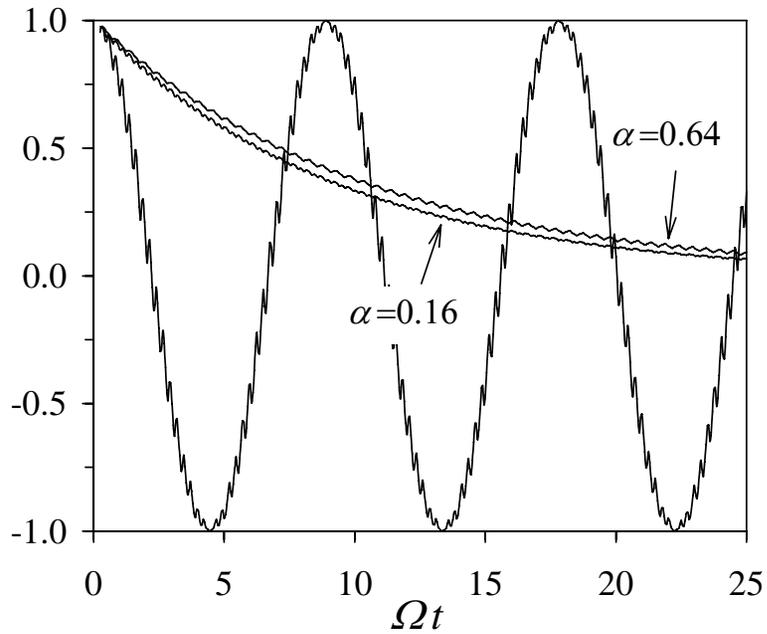
Can one control the charge oscillations?

- Maintain localization for indefinite time lengths?
- Sustain long-lived coherent oscillations?

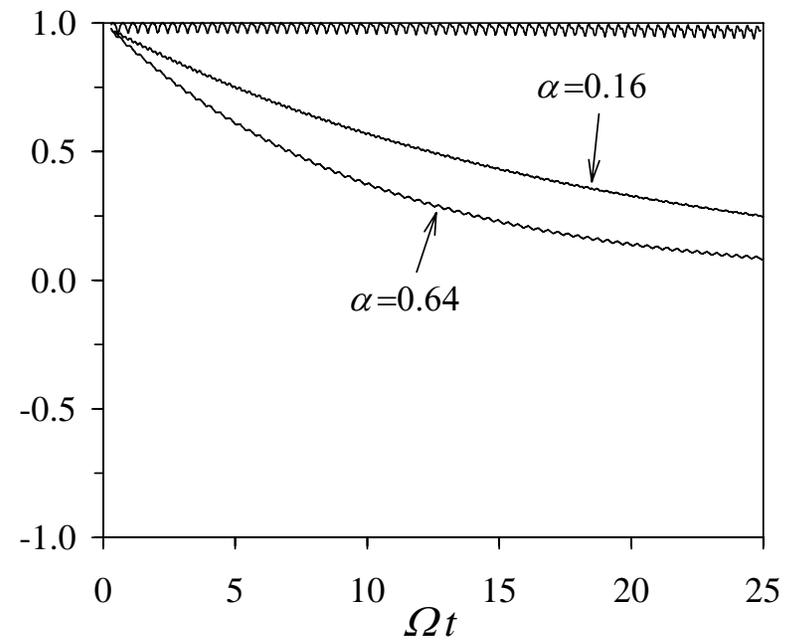
Localization at High Temperature

Average TLS position as a function of time

Generic field



Optimal field



References on Real-Time Path Integral Methodology

- N. Makri, *Chem. Phys. Lett.* **193**, 435 (1992).
M. Topaler and N. Makri, *Chem. Phys. Lett.* **210**, 448 (1993).
D. Makarov and N. Makri, *Chem. Phys. Lett.* **221**, 482 (1994).
G. Ilk and N. Makri, *J. Chem. Phys.* **101**, 6708 (1994).
N. Makri and D. E. Makarov, *J. Chem. Phys.* **102**, 4600 (1995).
N. Makri and D. E. Makarov, *J. Chem. Phys.* **102**, 4611 (1995).
N. Makri, *J. Math. Phys.* **36**, 2430 (1995).
E. Sim and N. Makri, *Chem. Phys. Lett.* **249**, 224-230 (1996).
E. Sim and N. Makri, *Comp. Phys. Commun.* **99**, 335-354 (1997).
N. Makri, *J. Phys. Chem.* **102**, 4414-4427 (1998).
N. Makri, *J. Phys. Chem.* **103**, 2823-2829 (1999).
N. Makri, *J. Chem. Phys.* **111**, 6164-6167 (1999).
J. Shao and N. Makri, *Chem. Phys.* **268**, 1-10 (2001).
J. Shao and N. Makri, *J. Chem. Phys.* **116**, 507-514 (2002).

References on Applications

Transfer and relaxation rates

- M. Topaler and N. Makri, *J. Chem. Phys.* **97**, 9001 (1992).
M. Topaler and N. Makri, *Chem. Phys. Lett.* **210**, 285 (1993).
D. E. Makarov and N. Makri, *Phys. Rev. A* **48**, 3626 (1993).
M. Topaler and N. Makri, *J. Chem. Phys.* **101**, 7500 (1994).
M. Topaler and N. Makri, *J. Phys. Chem.* **100**, 4430 (1996).
K. M. Forsythe and N. Makri, *J. Chem. Phys.* **108**, 6819-6828 (1998).
K. M. Forsythe and N. Makri, *J. Mol. Structure* **466**, 103-110 (1999).
K. Forsythe and N. Makri, *Phys. Rev. B* **60**, 972-978 (1999).

Control of dissipative tunneling

- D. E. Makarov and N. Makri, *Phys. Rev. E* **52**, 5863 (1995).
D. E. Makarov and N. Makri, *Phys. Rev. B* **52**, R2257 (1995).
N. Makri and L. Wei, *Phys. Rev. E* **55**, 2475-2479 (1997).
N. Makri, *J. Chem. Phys.* **106**, 2286-2297 (1997).
G. Taft and N. Makri, *J. Phys. B* **31**, 209-226 (1998).
K. Dong and N. Makri, *Chem. Phys.* **296**, 273-279 (2004).
K. Dong and N. Makri, *Phys. Rev. A* **70**, 042101 (2004).
K. Dong and N. Makri, *J. Chem. Phys.* (submitted)

Biological electron transfer

- N. Makri, E. Sim, D. E. Makarov and M. Topaler, *Proc. Natl. Acad. Sci. U.S.A.* **93**, 3926 (1996).
E. Sim and N. Makri, *J. Phys. Chem.* **101**, 5446-5458 (1997).
J. Ray and N. Makri, *J. Phys. Chem.* **103**, 9417-9422 (1999).