# **Quantum-Classical Path Integral**

A Rigorous Formulation of Condensed Phase Dynamics

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#### Quantum-(Semi)Classical Dynamics: A very old puzzle

Treat a small (1d or 2d) quantum system embedded in a polyatomic environment whose dynamics can be captured through classical trajectories.

Combining a wavefunction-based treatment of the system with a classical treatment of the environment is inconsistent (Ehrenfest force). Many possible models:

- Pechukas method
- Surface hopping
- Multiple spawning

. . .

Quantum Liouville equation

The root of the problem:

Trajectories are local, wavefunctions are delocalized.

## Feynman's Path Integral Formulation of Time-Dependent Quantum Mechanics



- Number of grid points  $n \sim M^d$  astronomical number of terms
- Phase interference "sign problem"

# Quantum-Classical Path Integral (QCPI)

Express the propagators for the dynamical property of interest in path integral form and apply the stationary phase approximation with respect to the degrees of freedom of the environment.

N. Makri and K. Thompson, Chem. Phys. Lett. 291, 101 (1998). R. Lambert and N. Makri, *J. Chem. Phys.* **137**, 22A552 (2012).

For the (few) quantum degrees of freedom, sum over *all* paths. For the (many) classical degrees of freedom, include only *classical* paths.

The QCPI representation offers a unique advantage:

Paths are *local*, just like trajectories, so there is no averaging with respect to delocalized wavefunctions.

The quantum particle exerts a force on the classical particle which determines its trajectory. The classical particle modifies the action of the quantum particle, thus changing the quantum mechanical amplitude.

No assumptions or approximations required.

# **Basic QCPI Formulation**

$$\hat{H} = H_0(\hat{s}, \hat{p}_s) + T_{env}(\hat{\mathbf{p}}) + V(\hat{s}, \hat{\mathbf{q}}) \equiv H_0(\hat{s}, \hat{p}_s) + H_{env}(\hat{s}, \hat{\mathbf{q}}, \hat{\mathbf{p}})$$

s: system, q: environment

Path integral representation of the reduced density matrix:

- contains the effects of the environment on the system
- describes dynamics of environment under force exerted by system
- to be evaluated using classical trajectories

#### Classical trajectory approximations for influence functional

Forward-backward semiclassical (FBSD): stationary phase trajectories experience different forces along forward and backward system paths

mos

least

$$F^{\text{FBSD}}[s^{\pm}] = \int dx_0 \int dp_0 D^{\text{FBSD}}(q_0, p_0; [s^{\pm}]) e^{i\Phi_b^{\text{FBSD}}(q_0, p_0; [s^{\pm}])/\hbar}$$
$$D^{\text{FBSD}}(q_0, p_0; [s^{\pm}]) = C(q_0, p_0) \left\langle s_0^+ q_0 p_0 \right| \hat{\rho}(0) \left| s_0^- q_f p_f \right\rangle$$

N. Makri and K. Thompson, Chem. Phys. Lett. 291, 101 (1998).

Full semiclassical representation of each evolution operator: distinct trajectories

$${}^{\rm SC}[s^{\pm}] = \int dq_0 \int dp_0 \int dq'_0 \int dp'_0 D^{\rm SC}(q_0, p_0, q'_0, p'_0; [s^{\pm}]) e^{i\Phi_{\rm b}^{\rm SC}(q_0, p_0, q'_0, p'_0; [s^{\pm}])/\hbar}$$

Miller's double semiclassical initial value representation of bath dynamics

Quasiclassical: trajectory experiences average of forces along forward & backward system paths  $r_{class} = \frac{1}{2} \int dr \int dr r_{class} dr r_{class$ 

 $F_{\rm coh}^{\rm class}[s^{\pm}] \simeq \int dq_0 \int dp_0 \, D_{\rm coh}^{\rm class}(q_0, p_0; s_0^{\pm}) e^{i\Phi_b^{\rm class}(q_0, p_0; [s^{\pm}])/\hbar}$   $D_{\rm coh}^{\rm class}(x_0, p_0; s_0^{\pm}) = (2\pi\hbar)^{-1} \left( \left\langle s_0^+ q_0 p_0 \middle| \hat{\rho}(0) \middle| s_0^- q_0 p_0 \right\rangle - 2\gamma \left\langle s_0^+ q_0 p_0 \middle| (\hat{q} - q_0) \hat{\rho}(0) (\hat{q} - q_0) \middle| s_0^- q_0 p_0 \right\rangle \right)$ 

similar to derivative-FBSD - J. Shao and N. Makri, J. Phys. Chem. A **103**, 7753 (1999).

$$F_{\text{Wigner}}^{\text{class}}[s^{\pm}] = \int dq_0 \int dp_0 D_{\text{Wigner}}^{\text{class}}(q_0, p_0; s_0^{\pm}) e^{i\Phi_b^{\text{class}}(q_0, p_0; [s^{\pm}])/\hbar}$$

Miller's linearized semiclassical approximation applied to bath - Q. Shi and E. Geva, J. Chem. Phys. 121, 3393 (2004); J. A. Poulsen, G. Nyman, and P. J. Rossky, J. Chem. Phys. 119, 12179 (2003).

# System dynamics

Full discretized path integral (sum over all paths). All quantum interference, tunneling, etc. captured exactly.

# **Solvent dynamics**

Semiclassical (stationary phase) dynamics involves classical trajectories and a phase space distribution, which may be fully quantized:

$$F = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) e^{\frac{i}{\hbar} \Phi_{\text{env}}(\mathbf{q}_0, \mathbf{p}_0; s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm})}$$

$$\uparrow$$
phase space distribution

Boltzmann, Wigner of coherent state distribution, depending on the level of treatment; full imaginary-time path integral which may include boson exchange

# Special case: harmonic bath (spin-boson Hamiltonian)

For a system linearly coupled to a harmonic bath,

$$\hat{V} = \sum_{j} \left( \frac{1}{2} m \omega_j^2 \hat{q}_j^2 - c_j \hat{s} \hat{q}_j \right)$$

the phase space integral gives the exact Feynman-Vernon influence functional

$$F = \exp\left[-\frac{1}{\hbar}\int_{0}^{t} dt' \int_{0}^{t'} dt'' \left[s^{+}(t') - s^{-}(t')\right] \left[\alpha(t' - t'')s^{+}(t'') - \alpha(t' - t'')^{*}s^{-}(t'')\right]\right]$$

and QCPI produces the full quantum mechanical result. QCPI offers an alternative to the i-QuAPI methodology [Makri group - 1990s].



How good is the classical trajectory treatment (with a quantized density) for an anharmonic fluid?

# **FBSD simulation of normal and superfluid helium** Dynamic structure factor: FBSD vs. neutron scattering



o Bose-Einstein condensation

The increase in the peak height is a consequence of confinement due to BEC. A. Nakayama and N. Makri, *Proc. Nat. Acad. Sci. U.S.A.* **102**, 4230-4234 (2005).

# **Basic structure of QCPI**

$$\rho_{\rm red}(s_N^{\pm};t) = \sum_{s_0^{\pm}} \sum_{s_1^{\pm}} \cdots \sum_{s_{N-1}^{\pm}} e^{\frac{i}{\hbar} \Phi_0(s_0^{\pm}, \dots, s_N^{\pm})} \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) e^{\frac{i}{\hbar} \Phi_{\rm env}(\mathbf{q}_0, \mathbf{p}_0; s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm})} \\
= \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) \sum_{s_0^{\pm}} \sum_{s_1^{\pm}} \cdots \sum_{s_{N-1}^{\pm}} e^{\frac{i}{\hbar} \Phi_0(s_0^{\pm}, \dots, s_N^{\pm})} e^{\frac{i}{\hbar} \int_0^t \Delta V_{\rm env}(\mathbf{q}(t); s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm})} dt'$$

Each classical trajectory supplies a phase which modifies the amplitude of the quantum system along the particular quantum path. *All the effects of the solvent on the system arise from this phase.* 

The quantum system 'drives' the solvent; i.e., the instantaneous position (state) of the system along one of its paths determines the force on the solvent trajectory. This is the 'back reaction'. Thus, for each initial condition of the solvent phase space, there is a different trajectory along each system path. (The trajectory "hops" according to state sequences specified by a path of the system.)

Neglecting the back reaction, i.e. assuming that there is a single trajectory from each initial condition, one recovers the old 'classical path' approximation.

$$\rho_{\rm red}(s_N^{\pm};t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0,\mathbf{p}_0) \sum_{s_0^{\pm}} \sum_{s_1^{\pm}} \cdots \sum_{s_{N-1}^{\pm}} e^{\frac{i}{\hbar} \Phi_0(s_0^{\pm},\dots,s_N^{\pm})} e^{\frac{i}{\hbar} \int_0^t \Delta V_{\rm env}(\mathbf{q}(t);s_0^{\pm},s_1^{\pm},\dots,s_N^{\pm}) dt'}$$

where q(t') also depends on the system path.

- Phase space integral evaluated by Monte Carlo.
- Sum over system paths evaluated explicitly (exactly).

The sum over system paths smoothes the phase, so Monte Carlo does not encounter a severe sign problem. Typical calculations use a few thousand initial conditions.



#### Full QCPI requires *n*<sup>2</sup> trajectories!

$$\rho_{\text{red}}(s_N^{\pm};t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0,\mathbf{p}_0) \sum_{s_0^{\pm}} \sum_{s_1^{\pm}} \cdots \sum_{s_{N-1}^{\pm}} e^{\frac{i}{\hbar} \Phi_0(s_0^{\pm},\dots,s_N^{\pm})} e^{\frac{i}{\hbar} \int_0^t \Delta V_{\text{env}}(\mathbf{q}(t);s_0^{\pm},s_1^{\pm},\dots,s_N^{\pm}) dt'}$$

There are  $(n^2)^{t/\Delta t}$  trajectories from each initial condition (all possible hops). This is the quantum-classical manifestation of nonlocality).

For a 2-state (donor "D" and acceptor "A") charge transfer reaction, in order to propagate by 1000 time steps, one must integrate 4<sup>1000</sup> solvent trajectories for each sampled initial condition.

DDDDDDDDDD... DADDDDDDDD... DDADDDDDDDD...

DDAADDDDDDD... DDADADDDDDD... DDADDADDDDD...



Can we make evaluation possible by exploiting the physics?

# The Mechanism of Decoherence



How does the solvent quench coherence?

## **1.** Pre-treatment of classical decoherence

#### Two contributions to the system-solvent interaction

A single solvent trajectory from each initial condition (i.e. a trajectory that neglects the state changes of the quantum system) defines a "classical path" approximation.

The "ensemble-averaged classical path" (EACP) can be shown to capture all effects associated with absorption and stimulated emission of phonons. These effects are dominant at high temperature. We refer to these effects as



N. Makri, Chem. Phys. Lett. 593, 93-103 (2014)

All other classical trajectories result from the changes of system state along each quantum path (the "back reaction"). These trajectories are responsible for spontaneous phonon emission (the "quantum decoherence"), which is essential for detailed balance.

#### Contributions of classical and quantum decoherence

#### Symmetric TLS



Red: classical decoherence only Blue: quantum decoherence only Black: both mechanisms (exact evolution)

For solvent degrees of freedom that have frequencies  $\hbar \omega \leq k_B T$ , classical decoherence dominates the dynamics.

#### Contributions of classical and quantum decoherence

Asymmetric TLS low temperature



Quantum decoherence is essential for detailed balance!

#### The good news:

All classical decoherence can be accounted for exactly in a single-step propagator for an augmented, time-dependent system Hamiltonian (where the time dependence arises from the solvent trajectory). Its calculation requires very little effort (a single solvent trajectory, along with integration of the Schrödinger equation for the time-dependent system Hamiltonian).

#### The bad news:

Inclusion of quantum decoherence requires evaluation of the full path sum.

## Exploiting classical decoherence

- Pre-treat the most important classical decoherence; i.e., incorporate all classical decoherence via system-independent (e.g., fixed charge or Ehrenfest) solvent trajectories into effective system propagators that capture (in each path integral step) the bulk of the effects induced by the solvent on the system, thus these effective propagators are valid for much larger time steps.
- Perform the full path sum to add the effects of quantum decoherence.

$$\left\langle s_0^{\pm} \left| \hat{\rho}_{\text{red}}(t) \right| s_0^{-} \right\rangle$$

$$= \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) \sum_{s_0^{\pm}} \sum_{s_1^{\pm}} \cdots \sum_{s_N^{\pm}} K^{\text{eff}}(s_0^{\pm}, s_1^{\pm}) \cdots K^{\text{eff}}(s_{N-1}^{\pm}, s_N^{\pm}) e^{i\Delta\Phi_{\text{env}}(\mathbf{q}(t); s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm})/\hbar}$$

Still  $n^{2N}$  trajectories per initial condition, but *N* is now much smaller.

this phase corrects the EACP propagators by adding the quantum decoherence 2. Decay of quantum-classical memory and iterative decomposition of QCPI

## Decoherence leads to memory quenching

Interactions with degrees of freedom not treated explicitly lead to memory effects (e.g. the generalized Langevin equation).

Because of destructive phase interference, the memory arising from condensed phase environments has a finite length.

In the QCPI context, memory manifests itself in the dependence of classical trajectories on the history of the quantum path, i.e. the sequence of states that determined the forces. This memory is associated with the quantum mechanism of decoherence.

It follows that decoherence implies (upon averaging) a lack of sensitivity of trajectory evolution to the precise nature of the quantum path in the distant past.

The precise force exerted by the system beyond its recent history (the "quantum decoherence time") is not important to the averaged solvent dynamics. We choose one of the trajectory branches in the pre-memory interval (free solvent branch, donor branch, random branch, dynamically consistent state hopping...). This way the number of trajectories is fixed and does not grow exponentially with propagation time. Also this leads to an iterative decomposition of QCPI (analogous to that in the i-QuAPI methodology).



- Note the classical memory is not truncated at all.
- Convergence with respect to the quantum memory length included yields full QCPI results.

R. Lambert and N. Makri, *J. Chem. Phys.* 137, 22A553 (2012) P. L. Walters and N. Makri, *J. Chem. Phys.* **144**, 044108 (2016)

Number of trajectories per initial condition reduced to  $n^{2L}$ , where *L* is the number of time steps that span the *quantum* memory length.

# The iterative QCPI calculation converges to the rigorous quantum-classical result.

$$H_0 = -\hbar\Omega\sigma_x + \varepsilon\sigma_z \qquad V = \sum_j \left(\frac{1}{2}m\omega_j^2 \hat{x}_j^2 - \sigma_z c_j \hat{x}_j\right)$$



R. Lambert and N. Makri, J. Chem. Phys. 137, 22A553 (2012).

## Charge Transfer in Solution: Ferrocene-Ferrocenium in Hexane









**Peter Walters** 

1,320 solvent atoms (periodic boundary conditions) with CHARMM force fields



# Convergence of all-atom QCPI



#### solvent delocalization

### Non-exponential kinetics



## The harmonic bath mapping: A path integral derivation



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

The influence functional can be expressed as a cumulant expansion:

$$F\left(s_{0}^{\pm}, s_{1}^{\pm}, \dots, s_{N}^{\pm}\right) = \exp\left\{-\sum_{k_{1}=0}^{N} \left(\alpha_{k_{1}}^{+} s_{k_{1}}^{+} + \alpha_{k_{1}}^{-} s_{k_{1}}^{-}\right) - \sum_{k_{1}=0}^{N} \sum_{k_{2}=0}^{N} \left(\beta_{k_{1}k_{2}}^{++} s_{k_{1}}^{+} s_{k_{2}}^{+} + \beta_{k_{1}k_{2}}^{+-} s_{k_{1}}^{+} s_{k_{2}}^{-} + \cdots\right) - \sum_{k_{1}=0}^{N} \sum_{k_{2}=0}^{N} \sum_{k_{2}=0}^{N} \left(\gamma_{k_{1}k_{2}k_{3}}^{++++} s_{k_{1}k_{2}}^{+} s_{k_{3}}^{+} + \gamma_{k_{1}k_{2}k_{3}}^{+++-} s_{k_{1}k_{2}}^{+} s_{k_{3}}^{-} + \cdots\right) - \cdots\right\}$$

It can be shown that the various coefficients are given by multi-time correlation functions of the bath; further, if the interaction affects an infinite number of bath coordinates uniformly, the influence functional is Gaussian, i.e., there is an *effective* harmonic bath of fictitious degrees of freedom which gives rise to the same system dynamics.

$$J(\omega) = \beta \omega \int_0^\infty C_{\rm ff}(t) \cos(\omega t) dt$$

#### Effective harmonic bath dynamics



**3.** Quadratic treatment of quantum decoherence

## Quantum decoherence is a 'vacuum' effect

Quantum decoherence is important at low temperatures/energies, where potential energy surfaces are nearly harmonic. This allows an efficient, cumulative treatment of the back reaction, which requires *a single* classical trajectory per initial condition. This allows QCPI calculations with MD efficiency!

N. Makri, *Faraday Discuss.* **195**, 8192 (2016). F. Wang and N. Makri, in preparation.

Full QCPI dynamics vs. quadratic treatment of quantum decoherence for ferroceneferrocenium electron transfer in hexane



## 4. Blip decomposition of QCPI

Blips are time segments where the forward and backward system paths are not identical.

- Classical decoherence decreases exponentially the contribution of multi-blip paths.
- Most natural and efficient approach for incoherent dynamics.



Sum over paths can be replaced by sum over blips. Between-blip contributions can be obtained by *Markovian* procedures.



- Exponential acceleration of the path sum.
- Minimal effort with very long memory!



N. Makri, J. Chem. Phys. 141, 134117 (2014); 146, 134101 (2017); Faraday Discuss. 195, 8192 (2016)

# Effects of solvent polarity

Investigate the exponential/non-exponential character of the dynamics, the charge transfer rate, and the accuracy of the harmonic bath mapping for a series of solvents with increasing polarity (and reorganization energy  $\lambda$ ).

	hexane
	trans 2-hexene
λ	piperylene (1,3-pentadiene)
	benzene
	methanol

## **Non-Equilibrium Reactive Flux**

For slow reactions, one would like to calculate the rate, rather than simulating the complete transformation of reactants into products. This is done using the reactive flux correlation function formalism, which evaluates the flux (with the equilibrium initial density) up to the "plateau time". However,

- Some reactions exhibit nonexponential kinetics, thus the long-time rate is not very meaningful.
- The existence of a "plateau" requires a true separation of timescales. For fast reactions it may not be possible to extract a rate from the standard flux expression.
- The conventional quantum flux correlation function formalism is not directly amenable to quantum-classical treatments.

The non-equilibrium formulation of the reactive flux is applicable to slow and fast reactions and directly adaptable to quantum-classical representations.

A.Bose and N. Makri, JCP (under review)

#### Hexane



non-exponential dynamics

#### Trans 2-hexene



#### Piperylene



A. Bose, P. L. Walters and N. Makri, to be submitted

#### Benzene



### Summary of QCPI methodology

QCPI is a rigorous quantum-classical formulation. It makes no *ad hoc* assumptions and uses no adjustable parameters. Yet there is no sign problem.

Zero-point energy effects for the classical particles can be included, if desired, by using the Wigner phase space density.

Quantum interference effects are fully included through the superposition of phases, which include the interaction between quantum and classical degrees of freedom. Quantum delocalization spreads to the classical particles.

All decoherence effects are accurately accounted for through these phases. There is no need for externally introduced 'decoherence terms'.

QCPI rigorously satisfies detailed balance through phases associated with spontaneous phonon emission. At long times, state populations attain the correct thermodynamic values.

QCPI is exact for a system coupled to a harmonic bath.

The QCPI algorithm can be used with thousands of atoms, described in full detail via available force fields or *ab initio* electronic structure.

External time-dependent fields and Langevin thermostats are easily included.

The method is characterized by MD scaling and is easily parallelizable.



Salut

CARRY MANAGER

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